CENTRAL VALLEY REGIONAL
WATER QUALITY CONTROL BOARD

RELATIVE RISK EVALUATION FOR PESTICIDES USED IN THE SACRAMENTO RIVER WATERSHED

DRAFT - REVISED

February 2006

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

State of California
Arnold Schwarzenegger, Governor

California Environmental Protection Agency
Dr. Alan Lloyd, Ph.D., Secretary

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

11020 Sun Center Drive #200
Rancho Cordova, CA 95670

Phone: (916) 464-3291
eMail: info5@waterboards.ca.gov
Web site: http://www.waterboards.ca.gov/centralvalley/

RELATIVE RISK EVALUATION FOR PESTICIDES USED IN THE SACRAMENTO RIVER WATERSHED

DRAFT - Revised

February 2006

REPORT PREPARED BY:

Zhimin Lu, Ph.D.
Gene Davis
Joe Karkoski

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

This page intentionally left blank.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

APPENDIX

1. Introduction

Agricultural and commercial applications of more than three hundred pesticides are reported annually for the Sacramento River watershed (DPR, 2003a). Several of these pesticides are included in the Clean Water Act Section 303(d) list for California waterways (SWRCB, 2003) and, therefore, are scheduled for total maximum daily load (TMDL) development. The objective of this report is to evaluate the relative risks of selected (target) pesticides to impact surface water quality in the Sacramento River watershed. This report presents a methodology for evaluating available data for pesticides that have the highest amount of use or have been detected in surface waters. Further, this evaluation presents a relative risk ranking approach for evaluating the overall relative risk of each 'target' pesticide to impact aquatic organisms (either animals or plants). For those pesticides with high overall relative risk, additional evaluation will be conducted to determine whether the adoption of water quality objectives or other action is necessary.

1.1 Review of Previous Pesticide Risk Evaluations

In the 1980s, two projects conducted by the State Water Resource Control Board (SWRCB) and the Central Regional Water Quality Control Board (CRWQCB) assessed the risks of two rice herbicides (molinate and thiobencarb) to the Sacramento River water system (SWRCB, 1984; SWRCB, 1990). The reports reviewed the existing monitoring data, evaluated toxicity data for aquatic species, determined the water quality criteria for the rice pesticides, and recommended control measures for reducing pesticide discharges from rice fields.

A more recent study assessed the risk of pesticides to the Sacramento-San Joaquin Delta (Delta; Kuivila, et al., 2004). The study described two methods for ranking the risks to surface waters of pesticides used or detected in the Delta. One method was applicable to pesticides for which measured concentration data in surface water and toxicity values are available. Pesticides were ranked into one of three levels according to the ratio of their measured concentrations to their respective toxicity values. Higher ratios indicate relatively higher risk to surface waters. The other method was for pesticides that have no associated surface water concentration data. These pesticides were ranked based on a combination of scoring parameters including their relative amounts of agricultural use, water solubility values, hydrolysis rate values, and volatility values. Over 160 pesticides were evaluated using one of these two methods. Approximately 35% of the pesticides were ranked using the ratio of measured concentration levels to toxicity value, approximately 40% of the pesticides were ranked using the combination of scoring parameters method, and approximately 25% of the pesticides were not ranked using either method because of insufficient data.

Over the past decade the California Department of Pesticide Regulation (DPR) has evaluated the environmental fates of 35 pesticides (DPR, 2004). The evaluation reports describe the chemical and physical properties of the pesticides and their measured concentrations in air, soil, and water. To protect fish and wildlife, the California Department of Fish and Game (CDFG) assessed the risks of 20 pesticides to impact freshwater and saltwater aquatic organisms (CDFG, 2003). The CDFG evaluated the available toxicity data and proposed water quality criteria (WQC) based on guidelines prepared by the United States Environmental Protection Agency (USEPA). However, WQC were proposed by CDFG for only a few pesticides because of insufficient information for the majority of pesticides.

2. Overview of data sources

Information used for this relative risk evaluation report includes the chemical and physical characteristics of pesticides in water and sediment, acute toxicity values to aquatic organisms from to exposure to the pesticides, total monthly pesticide use patterns, major crops on which pesticides are applied, and concentrations of pesticides measured within surface waterways in the Sacramento River watershed.

The major sources of data used for the relative risk evaluation include: pesticide chemical and physical properties databases (Oregon State University [OSU], 1994; Agricultural Research Service [ARS], 2003; and EXTOXNET, 2003); a pesticide use database (PUR database, DPR, 2003a); a pesticide toxicity database, "EcoToxicity" (USEPA, 2003); and a database of pesticide concentrations measured in surface water (SWDB; DPR, 2003b).

The chemical and physical properties values typically range widely because of different testing conditions associated with each data source. The ARS pesticides properties database (ARS, 2003) was developed for predicting the potentials of pesticides to move into groundwater and surface water. The ARS database includes values for 16 chemical and physical properties for over 300 pesticides. The database includes original values and references and also provides suggested values for modeling purposes when multiple values are listed.

The OSU pesticides properties database presents water solubility values, soil sorption coefficients (Koc), and soil half-life values (OSU, 1994). Most of the pesticide property values were adapted from the ARS database. For this relative risk study, the OSU database was selected as the main data source for the chemical and physical characteristics because it contains the three main parameters used in evaluating the relative risks of the 'target' pesticides. The pesticide property values were confirmed using the data from the EXTOXNET database (EXTOXNET, 2003), which was supported by: the Cooperative Extension Offices of Cornell University, Michigan State University; Oregon State University; and the University of California at Davis. The EXTOXNET database also describes the environmental fates and toxicities of the pesticides.

The PUR database (DPR, 2003a) includes the records of individual applications of registered pesticides used for agricultural purposes in California. This study used PUR data from 1992 to 2001 for the Sacramento River watershed to calculate the amounts (by pounds applied and by acreages applied to) of pesticide applications on different crops by month and year of application. Pesticides with high application amounts were selected as 'target' pesticides for relative risk evaluation, as summarized in this report.

The USEPA EcoToxicity database contains over 14,000 acute and chronic pesticide toxicity test results using aquatic invertebrates, amphibians, fish, plants, insects, and birds as test species (USEPA, 2003). The pesticides with the lowest 96-hour lethal concentration to 50% of the test organisms (LC50) or the lowest effect concentration to 50% of the test organisms (EC50), based on toxicity test using aquatic animals (aquatic invertebrates, amphibians, and fish) and the lowest EC50 values, based on toxicity testing using aquatic plants, were used in ranking relative risks. The database has been reviewed by the USEPA Ecological Effects Branch biologists and deemed by them to be acceptable for use in the ecological risk assessment process (USEPA, 2003).

Surface water pesticide concentration data for the eight counties (Butte, Colusa, Glenn, Sacramento, Solano, Sutter, Yolo, and Yuba) that encompass the lower Sacramento River watershed was also considered when evaluating the overall relative risk for pesticides to impact surface waters in the Sacramento River watershed. The major source for this data is DPR's Surface Water Database (SWDB; DPR, 2003b).

3. Methodology

Target pesticides were identified and ranked according to their potential relative risks to impact aquatic organisms in surface water (Figure 1).

3.1. Target pesticides identification

Three steps were used to select the target pesticides. Step 1 was to select the 30 pesticides that were applied in the highest amounts (pounds of pesticide applied) and, separately, the 30 pesticides that were applied to the greatest total areas (acres), for each year from 1992 to 2001 (DPR, 2003a). Thus, a total of 20 lists (two per each year) of pesticides were generated for the ten-year period. Step 2 was to combine the pesticides identified in the 20 lists (from Step 1) into a single list. Step 3 was to narrow the list of pesticides (from Step 2) into a list of 'target' pesticides by: removing the pesticides that have very low toxicity (the lowest 96-hour LC50 value is >100,000 micrograms per liter[µg/L]) to aquatic organisms (e.g. sulfur); the chemicals used as adjuvants or solvents for the actual pesticides that were applied (e.g. mineral oil); and the pesticides without any available 96-hour or 48-hour LC50 or EC50 toxicity data (e.g. copper ammonium complex).

The initial target pesticides list included 71 pesticides (Table 1), which accounted for 90% of the annual pesticide use in terms of weight (by pounds applied) and 60% of the annual pesticide use in terms of area (by acres) for the Sacramento Valley. Although sulfur has the highest amount of use (approximately 30% of total annual pesticide use, by weight), it was removed from the target list of pesticides because of its low toxicity values. After excluding sulfur from the list, the other target pesticides accounted for approximately 60% of the total annual pesticide use, by weight. In terms of the acreage to which sulfur was applied, it accounted for only 1.45% of the total reported pesticide use in 2000. After similarly excluding other low toxicity pesticides, the total acreage to which the remaining target pesticides were applied still accounted for over 50% of annual reported pesticide use in the Sacramento Valley. The initial target pesticide list included the pesticides that were reportedly used the most in the Sacramento valley.

The initial target pesticides list was refined to a target list containing 48 pesticides (Table 2). Four of the pesticides – atrazine, diuron, norflurazon, and simazine - not identified in the initial target list were added to the target list based on DPR staff recommendations, since the four pesticides have been detected in surface water samples collected from Sacramento River watershed waterways (Sanders, 2005).

3.2. Relative risk evaluation

Among the 48 target pesticides, 23 were evaluated and reviewed by the Central Valley Regional Water Quality Control Board (CVRWQCB), the DPR, or the CDFG. Seven pesticides are on the 303(d) list (CVRWQCB, 2003). Fourteen pesticides were evaluated by the CDFG for hazard assessments to aquatic organisms (CDFG, 2004) and 14 pesticides were evaluated for environmental fate by the DPR (DPR, 2004). The 48 target pesticides were evaluated using a relative risk approach, described briefly below. Following the evaluation approach summary, the results of the evaluation are summarized below for each target pesticide.

The relative risks of pesticides to impact surface water quality can be determined based on many considerations. However, the consideration of all possible factors that could influence the relative risk evaluations, including weather (rain, wind, temperature), hydrology (river travel time, water levels, irrigation drainage patterns), geography (land slope, distance from point of application to surface water), human management (irrigation and drainage system operations), and the spatial and frequency distributions of pesticide applications, were beyond the scope of this study.

The parameters considered in this study for evaluating and ranking the overall relative risk of each target pesticide to impact surface water quality include toxicity to aquatic organisms and chemical and physical properties - mainly water solubility values, soil absorption coefficient (Koc) values, and half-life in soil values. Ranges of values for each parameter were defined and assigned to one of five levels: very low, low, moderate, high, and very high (Table 3). Total annual and monthly pesticide reported use patterns (DPR, 2003a), the associated relative risk to impact surface water quality via field runoff due to the timing of pesticide application, and the available surface water monitoring pesticide concentration data were also used in determining the overall relative risk ranking for target pesticides.

Toxicity to aquatic organisms is a crucial factor in determining the overall relative risk of a pesticide to impact surface water quality. The smaller a pesticide's LC50 or EC50 toxicity value, the higher its relative toxicity. For insecticides and fungicides, the lowest acute toxicity values (96-hour or 48-hour LC50 or EC50, from the EcoToxicity database) tested on the most sensitive species of aquatic animals were used to determine a relative risk ranking level due to toxicity. For most herbicides, the lowest 5-day or 4-day EC50 value, based on toxicity testing using aquatic plants, were included in the relative risk ranking level due to toxicity. The selected lowest toxicity values, the ranges of toxicity value ranking levels, and the application season (months) are listed in Table 4. If the lowest EC50 value tested on aquatic plants was lower than the LC50/EC50 tested on aquatic animals, the lowest EC50 value for aquatic plants was used to determine the relative risk toxicity level rank. The lowest toxicity values of target pesticides ranged from 0.0041 to 1,000,000 micrograms per liter (μg/L) and were ranked into one of (Table 3)

Water solubility values indicate how much pesticide can be dissolved in a specified amount of water (at relatively typical environmental conditions). In general, the lower the water solubility value, the lower the risk for the pesticide to impact surface water quality directly. However, some pesticides (e.g., chlorpyrifos) with low water solubility values still have high risk potential to indirectly impact aquatic organisms via exposure to contaminated sediments. The water solubility values of the target pesticides range from 0.0002 to 2,100,000 mg/L. Since this range of water solubility values is so large, the water solubility values for the individual target pesticides were assigned relative risk ranking levels based on the logarithms of the water solubility values (Table 3)

The unitless soil/sediment organic carbon water partitioning coefficient (Koc) value describes how strongly a chemical (e.g., pesticide) adheres to the organic fraction of soil relative to remaining dissolved in water. A high Koc value means the pesticide prefers to adsorb to sediment rather than stay dissolved in water. Koc values for the target pesticides ranged from 20 to 180,000, and were assigned to one of five relative risk-ranking levels (Table 3). When the Koc value of a pesticide is ranked as high or very high, the potential relative risk to impact surface water quality (directly affecting the health of aquatic organisms exposed to the contaminated sediment) is considered high.

The soil half-life values indicate how long pesticides are expected to persist in soil particles. In general, pesticides with shorter soil half-lives present less risk to aquatic organisms, as they would more quickly degrade to non-toxic levels. Soil half-life values of the target pesticides ranged from 1 to 650 days and were assigned to one of five relative risk-ranking levels.

Pesticide use report (PUR) data was used not only in the initial target selection process but also to identify trends in use of the target pesticides over a 10-year period (1992 to 2001). For each target pesticide, the total annual and total monthly reported use amounts were calculated. The total annual use amount trends indicate whether the amounts of the target pesticides used have decreased or increased over time. Pesticides that decreased significantly in annual total reported use amounts pose lower relative risk to aquatic organisms than those pesticides whose total annual reported use amounts increased over the same period.

The amount of use is an important factor in the relative risk determination, especially the amount used in more recent years. The total annual target pesticide use amounts, from

1998 to 2001, were calculated for all pesticides reportedly used to identify the 30 with the highest total amounts used (in terms of weight) and to identify the 30 pesticides with the highest total use amounts (in terms of acreage) to generate a four-year list. The target pesticides listed in the ten-year list (1992 to 2001) but not listed in the four-year list (1998 to 2001) were considered to have a lower relative risk to impact surface water quality.

The total monthly amounts of target pesticides reportedly used were evaluated to identify the potential for seasonal runoff. The winter storm season (December to March) and the summer irrigation season (April to August) are considered to have higher relative risks for pesticides to occur in field runoff than other seasons. Several studies indicated high amounts of organophosphate pesticide runoff from orchards during winter storms (Kuivila and Foe, 1995; Holmes, *et al.*, 2000; Nordmark *et al.*, 1998). Therefore, relatively high amounts of pesticide use during the winter storm season suggest relatively high risk for aquatic organisms to be exposed to pesticides.

The amount of water (and, potentially, pesticide) runoff from agricultural lands varies with soil type and moisture content, crop type, land slope, and irrigation technology. Currently, there is no information about the relationship between the type of crop and the amount of runoff to be expected. Therefore, the crop type was not used to evaluate runoff risk.

For the purposes of this report, target pesticide concentration data in the DPR surface water database (SWDB), for surface water samples collected in the Sacramento River watershed between 1992 and 2002, were used. For the target pesticides having concentration data in the SWDB, the highest concentration values were compared to the acute toxicity values of the given pesticides to assign them to overall relative risk ranks. Not all target pesticides have concentration data in the SWDB. The overall relative risk rank of a target pesticide is high if the observed maximum concentration exceeded the lowest toxicity value. Otherwise, the overall rank is moderate. For the pesticides without observed concentration data, the application season and overall trend of annual uses were used to determine the overall rank. If most of the applications occurred during the winter storm season (December to March), the overall risk can be high. Otherwise, the overall rank will be moderate. If the trend of annual uses decreased significantly in recent years, the overall risk can be ranked as moderate.

Each target pesticide was assigned to one of three overall relative risk levels - high, moderate, or low - based on the lowest 96-hour or 48-hour LC50 or EC50 value (using the most sensitive species of aquatic animals for toxicity testing) or based on the lowest 120-hour or 96-hour EC50 value (using aquatic plants for toxicity testing). The relative risk rank was a dominant factor in determining the overall relative risk rank. For the target pesticides with toxicity relative risk ranked as very high, moderate, and low, the overall relative risk ranks are high, moderate, and low, respectively (Figure 2). For the target pesticides with toxicity relative risk ranked as high, the overall rank could be either high or moderate. These target pesticides were further evaluated based on three factors -

observed concentrations, the months of application (relative to runoff potential), and/or trend of total annual reported use amounts (Figure 3).

The relative risk ranks associated with each target pesticide's toxicity, water solubility, Koc, and soil half-life values, and the overall relative risk ranking for each of the target pesticides, are listed in Tables 5A through Table 5C. The overall relative risk ranking includes 22 target pesticides in the "high" risk category (Table 5A), 18 target pesticides in the "moderate" risk category (Table 5B), and eight target pesticides in the "low" risk category (Table 5C). The nine pesticides excluded from the four-year list (1998 to 2001) are indicated in Tables 5A through 5C, and their overall relative risk ranks could be lower.

The relative risk for aquatic toxicity due to sediment-bound pesticides was ranked for each target pesticide, based on the relative risk rank of the Koc value. If a target pesticide has a "very high" or "high" relative risk Koc value ranking, the relative sediment risk of the target pesticide was ranked as "potential". If a target pesticide has a low or very low Koc value, its relative risk to contaminate sediment was ranked as "unlikely". If the target pesticide has a moderate Koc value, its relative risk to contaminate sediment was ranked as "possible".

For each target pesticide, a summary of relevant usage information, physical, chemical and toxicological properties, water quality data, and a concluding discussion of the overall relative risk ranking are presented in Appendices A through C.

4. Results and Discussion

The results of the overall relative risk evaluation for the target pesticides are presented and discussed below.

4.1. "High" Overall Relative Risk Pesticides

Of the 22 pesticides ranked as posing a high overall relative risk to impact surface water quality, six are herbicides, of which four were ranked as high risk because they are highly toxic to aquatic plants. The other two herbicides, thiobencarb and trifluralin, are ranked as high risk due to their relatively high toxicity to aquatic animals.

The 96-hour or 48-hour LC50 or EC50 values for the 22 high overall relative risk pesticides ranged from 0.0041 to 33 µg/L (Table 5A). One pesticide, (paraquat dichloride) has very high solubility in water. Five of the target pesticides are highly soluble in water (carbofuran, malathion, methidathion, molinate, and propanil). Six of the target pesticides are moderately soluble in water –(azinphos methyl, diazinon, diuron, methyl parathion, thiobencarb, and ziram). Ten of the target pesticides have low or very low water solubilities, but they also have high potentials to adsorb to soil/sediment particles. For the 10 pesticides with low water solubility, three are synthetic pyrethroids –(esfenvalerate, lambda cyhalothrin, and permethrin); the other seven are captan, chlorothalonil, chlorpyrifos, maneb, oxyfluorfen, propargite, and trifuralin. Four herbicides were evaluated as having high overall relative risk rankings due to their toxicity to aquatic plants (diuron, oxyfluorfen, paraquat dichloride, and propanil).

Paraquat dichloride is an herbicide with a high water solubility value (626,000 mg/L). It is highly toxic to aquatic plants but has relatively low toxicity to aquatic animals, like scud (a crustacean). There are no paraquat dichloride concentration data available in the SWDB for the Sacramento River watershed. The major reported applications of paraquat dichloride were to alfalfa fields, and to almond and pear orchards, from December to April. By 2001, the total annual use amounts had decreased to about 46% from their total annual reported use amounts in1997. Since paraquat dichloride also has a relatively very high Koc value and a long half-life in soil value, its relative risk to contaminate sediments is high (ranked as "potential").

Carbofuran, malathion, methidathion, molinate, and propanil have water solubility values ranging from 130 to 970 mg/L. Except for propanil, the total annual reported use amounts of these pesticides have decreased over recent years. Carbofuran, malathion, and methidathion were not included in the four-year list (the top 30 highest-use pesticides between 1998 and 2001). However, carbofuran, malathion, and molinate are included on the 303(d) list for causing impairment to several Sacramento River watershed waterways.

Carbofuran is an insecticide, acaricide, and nematicide. The majority of carbofuran applications were to rice fields. The use of granular formulations was reduced because of the high risk of toxicity to birds by ingestion. Carbofuran poses an overall relatively high risk to surface water quality (to impact aquatic organisms) because of its high toxicity and its high water solubility values. The highest carbofuran concentration measured exceeded the lowest toxicity value. The current overall relative risk may be lower because the total annual reported use amounts have decreased in recent years. The total annual reported use amount of carbofuran in 2001 was only 4% of the total annual reported use amount in 1993. As about 95% of carbofuran was applied to rice, the control of rice field discharge was critical in reducing the amount of carbofuran in the surface waters of the Sacramento River watershed. However, carbofuran is no longer used on rice fields (Federal Register: August 1, 2001, Volume 66, Number 148). The relative risk for carbofuran to contaminate sediments is ranked as "unlikely" because of its relatively low Koc value.

Malathion is an insecticide that is mainly applied to walnut orchards and to alfalfa and rice fields. High amounts of malathion are reportedly applied to crops between March and September with the highest total monthly reported use amounts in August and very low total monthly reported use amounts from October to February. The potential for malathion to occur in agricultural runoff is relatively high during the irrigation season. High concentrations of malathion were detected in surface water samples collected in May 1996. The highest observed concentration (6 µg/L; DPR, 2003a) was higher than the lowest toxicity value (0.5 µg/L) and much higher than the CDFG proposed CMC (0.43 µg/L). However, the current relative risk to impair surface water quality (impact aquatic organisms) from exposure to malathion could be lower than in the recent past because the reported amount used has decreased approximately 83% from 1992 to 2000.

Malathion has a relatively high Koc value, so it poses a "potential" relative risk to contaminate sediments.

Methidathion is an insecticide that is applied to orchards (prune, almond, peach, etc.) during the winter dormant/storm season. Because of the seasonality of use and the typical application method ("blast sprayer" aimed at bare trees), the potential for methidathion to occur in winter storm runoff from orchards is high. The overall relative risk to impair surface water quality (impact aquatic organisms) by the exposure to methidathion is high because the highest observed concentration (15.1 µg/L) was higher than the lowest acute toxicity value (0.7 µg/L). However, the current risk may be lower because the reported amounts used have decreased such that the total annual amount reportedly used in 2001 was only 7% of the total annual reported amount used in 1993. The CDFG assessed the risk to impact aquatic organisms, but water quality criteria were not proposed because of insufficient data (CDFG, 1995). There is also a moderate relative risk (ranked as "possible") for methidathion to contaminate sediments, based on its relatively high Koc value.

Molinate is an herbicide that is mainly applied to rice fields in May. Molinate is ranked as having a moderate relative risk to impair surface water quality (based on its toxicity values for aquatic animals and aquatic plants). However, it may pose a higher overall relative risk because it is often used with thiobencarb, creating a combined toxicity that is much higher than that of molinate itself. Molinate is also 303(d)-listed for several Sacramento River watershed waterways. The lowest 96-hour LC50 value for aquatic animals (760 µg/L) and the lowest EC50 value for aquatic plants (220 µg/L) based on the EPA EcoToxicity database (USEPA, 2003) Are higher than the CDFG-proposed water quality criterion (WQC; 13 µg/L) for the combined use of molinate and thiobencarb.

Propanil is an herbicide that is ranked as posing a high overall relative risk to impair surface water quality because of its high toxicity value for aquatic plants. It would be ranked as posing a moderate overall relative risk if the toxicity rank was based on the lowest 96-hour LC50 value for aquatic animals. The range of LC50 values for aquatic animals is from 400 to 16,000 µg/L. The most sensitive species to propanil exposure in surface waters is a mysid (*Mysidopsis bahia*). However, since the EC50 values for aquatic plants are much lower, ranging from 16 to 110 µg/L, the relative toxicity rank is high. In addition, the highest observed concentration in surface water (20.6 µg/L; DPR, 2003b), which is higher than the lowest EC50 value (16 µg/L) for aquatic plants. Therefore, the overall relative risk is ranked as high. The major applications of reported propanil use are on rice fields (99%) in May. The amount of use has reportedly increased in recent years. The lowest total annual reported amount used (13,789 lbs) was in 1992 and the highest total annual reported amount used (1,340,413 lbs) was in 2001. The relative risk for propanil to contaminate sediments is "possible" due to its Koc value.

Among the six pesticides ranked as posing a high overall relative risk to surface water quality, but with moderate water solubility values, three (diazinon, azinphos methyl, and methyl parathion) are included on the 303(d) list for causing impairment to several Sacramento River watershed waterways. A TMDL for diazinon in the Sacramento and

Feather Rivers has been prepared (Karkoski, 2003). Azinphos methyl has similar physical and chemical properties to diazinon, but the soil half-life of azinphos methyl is shorter and the primary application period is not during winter storm season, as for diazinon. Rather, the heaviest reported uses of azinphos methyl are to orchards during the irrigation season. The observed concentrations of azinphos methyl in water samples collected from surface water in the Sacramento River watershed were less than 0.06 µg/L, which is lower than the lowest toxicity value for azinphos methyl. The use of azinphos methyl has decreased about 81% from 1992 to 2001. From 1998 to 2001, the amount of azinphos methyl used was not in the top 30 highest use pesticides. Azinphos methyl has a relatively high Koc value and it may pose a "potential" risk to contaminate sediments.

Methyl parathion is an insecticide with a relatively moderate solubility value and that is mainly applied to orchards during the irrigation season. It is also included on the 303(d) list for Sacramento River watershed waterways. The annual total reported amount of methyl parathion used in 2001 was only 17% of the amount reportedly used in 1993, but the amount reportedly used in 2001 was higher than in 2000. Although methyl parathion was not included in the list of the highest 30 pesticides used from 1998 to 2001, surface water samples collected from the Sacramento River watershed contained methyl parathion at concentrations higher than the CDFG-proposed interim water quality criterion of 0.08 µg/L (CDFG, 2003). Therefore, DPR recommended that methyl parathion be added to the list of target pesticides (Sanders, 2005). The overall risk level may be lower considering that most of the applications do not occur during the winter storm season and the total annual amounts of use have generally decreased. There is a "potential" risk for methyl parathion to contaminate sediments because of its relatively high Koc value.

The other three pesticides with moderate water solubility (diuron, thiobencarb and ziram). Diuron is an herbicide that was not selected in the initial list because the amount of application was not in top 30 pesticides. The fate of diuron in the environment has been reviewed and CDPR staff has recommended that diuron be included in list of target pesticides because it has been detected in surface water samples (Sanders, 2005). The lowest 96-hour LC50 value for diuron was 160 µg/L, based on toxicity tests using scud. The lowest EC50 value was 2.4 µg/L, based on toxicity testing using green algae. The relative risk of toxicity is ranked as high based on this EC50 value. The overall relative risk is ranked as high because the highest observed concentration (30.6 µg/L) exceeded the lowest EC50 value (2.4 µg/L). Among 528 concentration data values, over 44% of them exceeded the limit of quantitation (LOQ) (0.05 to 1 µg/L). The major annual applications of diuron are on walnut orchards and alfalfa fields during the winter storm season. The total annual amounts of diuron reportedly used decreased slightly from 1999 to 2001. There is a "possible" risk for diuron to contaminate sediments based on its relatively moderate Koc value and its soil half-life value.

Thiobencarb is an herbicide that is used only on rice fields. The CDFG-proposed water quality criterion (WQC; 3.1 µg/L) is lower than the lowest 96-hour LC50 value (150 µg/L) for aquatic animals that was reported in the EXTOXNET database and it is also lower than the lowest EC50 value (17 µg/L) for aquatic plants that was recorded in the

USEPA toxicity database (USEPA, 2003). The main reason for CDFG to have proposed a low WQC value for thiobencarb is due to the combined effects of co-applications of thiobencarb with molinate. Thiobencarb is applied from April to June with the highest use in May. High concentrations (greater than the WQC of 3.1 µg/L) were observed in surface water samples collected in May and June. The total annual amounts of reported thiobencarb use have increased in recent years.

Ziram is a fungicide that is applied to orchards (e.g. almond, peach, and pear) between February and April, i.e. during the winter storm season. The CDFG evaluated the risk of ziram to impact aquatic organisms but no water quality criteria were determined because of insufficient data. Ziram is highly toxic to aquatic organisms with the lowest acute toxicity (96-hour LC50) being 8 µg/L. In recent years, the total annual amounts of ziram reportedly used have decreased, but ziram is still among the top 30 highest use pesticides. Therefore, there is still a potential risk for ziram to impair surface water quality. There is a "possible" risk for ziram to contaminate sediments, based on its relatively moderate Koc value.

Synthetic pyrethroid pesticides usually have relatively high toxicity, high Koc values, and low water solubility. Esfenvalerate, lambda cyhalothrin, and permethrin have relatively high total annual amounts (by acreage) of reported use. Other pyrethroid compounds (e.g. bifenthrin and cypermethrin) were not included in that list of target pesticides because of their low total annual amounts of reported use, but they have similar chemical and physical properties including high Koc values. The total annual amounts of esfenvalerate reportedly used increased from 1992 to 1998 and decreased slightly from 1998 to 2001. Esfenvalerate, lambda cyhalothrin, and permethrin with very high toxicities to aquatic organisms (96-hour LC50s range from 0.0041 to 0.07 µg/L) were included in the list of target pesticides. Because of their high Koc values, the relative risks for any of these three pyrethroids to sediments are ranked as "potential". Surface water samples collected in the Sacramento River watershed were analyzed for esfenvalerate, but it was not detected (DPR, 2003b). The relatively high total monthly amounts of reported use were in January and July. In January, esfenvalerate was mainly applied to orchards (e.g. prune and almond). In July, esfenvalerate was mainly applied to walnut orchards and tomato fields. There is potential risk of runoff from orchards to contain esfenvalerate during the winter storm season. Like other pyrethroids, esfenvalerate is difficult to detect in surface water samples, but it considered a "possible" risk to contaminate sediments.

Lambda cyhalothrin has reportedly been applied to crops since 1998 and the amounts reportedly used have increased since then. The relatively highest total monthly amounts of reported use were from May to July with the highest reported uses in May on rice and tomato fields (DPR, 2003a). The risk of lambda cyhalothrin to impair surface water quality is high during the irrigation season if field tailwater runoff occurs. However, there is no potential risk for lambda cyhalothrin to impair surface water quality during winter storms because there are almost no reported applications during the winter storm season.

The total annual amounts of permethrin reportedly used have decreased slightly since 1997. In 2001, the total annual amount of permethrin reportedly used was about 45% of the total annual amount reportedly used in 1997. The major reported uses were to peach, walnut, and almond orchards between May and August with the highest use on peach orchards in June. Since there were some reported permethrin applications during the winter storm season, permethrin may impair surface water quality if it is present in storm runoff.

Other synthetic pyrethroid compounds (e.g., bifenthrin and cypermethrin) could be ranked as posing high overall relative risks to impair surface water quality if their application amounts increase significantly in the future.

Seven other pesticides with low water solubility values and high Koc values that were ranked as posing high overall relative risks to impair surface water quality are chlorpyrifos, captan, chlorothalonil, maneb, oxyfluorfen, propargite, and trifuralin. Chlorpyrifos is included on the 303(d) list for some surface waters in the Sacramento River watershed and it was evaluated during the initial development of the Sacramento and Feather Rivers diazinon and orchard runoff TMDL (Karkoski, 2003). Chlorpyrifos is ranked as posing a high overall relative risk to impair surface water quality because its relative toxicity rank is "very high".

Captan is a fungicide with low water solubility, a moderate Koc value, and a very low soil half-life value (2.5 days). Captan is applied to prune, almond, and peach orchards in March, when there is still a possibility for winter storms to produce significant orchard runoff. The overall relative risk for captan to impair surface water quality may be lower because the total annual amounts reportedly used have decreased in recent years. The relative risk for captan to contaminate sediments is “possible” based on its relatively moderate Koc value. However, the overall relative risk for captan to contaminate sediments might be lower because of its relatively low half-life in soil value.

Chlorothalonil is a fungicide with a 96-hour LC50 of 26 μg/L for the most sensitive species. The highest reported amounts of chlorothalonil used were to tomato fields during the summer and the second highest reported amounts used were to prune orchards in March (DPR, 2003a). The total annual amounts of reported use have such that the total annual amount reportedly used in 2001 was only 14% of the total annual amount reportedly used in 1992. Surface water samples collected in the Sacramento River watershed from 1996 to 1998 were analyzed for chlorothalonil, and no concentrations were detected over the LOQs (0.035 and 0.48 μg/L). There is a “potential” risk for chlorothalonil to contaminate sediments, based on its relatively high Koc value.

Maneb is a fungicide that is mainly applied to walnut (73%) and almond (25%) orchards. Relatively high amounts of use were reported between February and May with the highest use in May. The 96-hour LC50 was 33 μg/L for the most sensitive species. From 1992 to 2001, the annual uses generally increased with the highest reduction of 46% except for 1999 and 2001. The annual uses in 1999 and 2001 were much lower than the uses in 1998 and 2000. The risk for maneb to contaminate sediments is "possible", based on its relatively moderate Koc value.

Oxyfluorfen is an herbicide that is mainly applied to orchards, such as almonds, prunes, walnuts, and pistachios during the winter storm/dormant season. The lowest 96-hour LC50 was 31.7 μg/L, based on toxicity testing using grass shrimp. The lowest EC50 tested on aquatic plants was 290 μg/L. The relative risk for oxyfluorfen to be present in winter runoff is high, but the current risk may be lower because the total annual reported amounts of use decreased from 1996 to 2001. There is a "potential" risk for oxyfluorfen to contaminate sediments based on its relatively high Koc value.

Propargite is an insecticide whose major applications are to almond and walnut orchards and to bean fields and cornfields between May and August. The highest total monthly amount reportedly used was in July and none was reportedly applied during the winter storm season. The lowest 96-hour LC50 was 31 μg/L. The relative risk of propargite to impact surface water quality is high because the total annual amounts reportedly used have increased from 1999 to 2001. The relative risk for propargite to contaminate sediments is "potential", based on its relatively high Koc value.

Trifluralin is an herbicide that is heavily applied to row crops such as tomato and alfalfa. Heavy use during the irrigation season (April to June) poses a relatively high risk of aquatic organism exposure to trifluralin via contaminated sediment. The lowest 96-hour LC50 was 8.4 μg/L tested on fish and the lowest EC50 (15.3 μg/L) value was tested on aquatic plants. Trifluralin has been detected in surface water samples with the highest observed concentration (0.023 μg/L) well below the lowest acute toxicity value. Trifluralin has a relatively high Koc value, so it poses a "potential" risk to contaminate sediments.

4.2. "Moderate" Overall Relative Risk Pesticides

Eighteen target pesticides are ranked as posing moderate overall relative risks to impair surface water quality (Table 5B). Among the 18 pesticides, eight have relatively high toxicity values (1.9 to 69.7 μg/L) and ten have moderate toxicity values (130 to 800 μg/L). The eight pesticides with relatively high toxicity are atrazine, carbaryl, copper oxide (ous), mancozeb, norflurazon, oryzalin, phosmet, and simazine.

Of the18 pesticides ranked as posing overall moderate risk to surface water quality, nine are herbicides. Most herbicides are more toxic to aquatic plants than to aquatic animals except for 2,4-D, dimethylamine salt and simazine. The three inorganic-copper components have different water solubilities. Copper oxide (ous) has much lower water solubility than copper sulfate (basic) and copper sulfate (pentahydrate). Three pesticides (2,4-D, dimethylamine salt; MCPA, dimethylamine salt; and metam-sodium) have relatively very high water solubility values.

Atrazine is an herbicide that was identified on the list of top 30 target pesticides (based on having high total amounts of reported use). Atrazine was added to the target pesticide list based on DPR's recommendation since atrazine has been detected in surface water samples (Sanders, 2005).. The mixture of atrazine with other pesticides (e.g. chlorpyrifos) increases the toxicities of the other pesticides. The 96-hour LC50 values range from 4,500 to 1,000,000 µg/L, based on toxicity testing using aquatic animals. The EC50 values, based on toxicity testing using aquatic plants, range from 22 to 460 µg/L. Over 1,000 concentration surface water samples collected in the Sacramento river watershed were analyzed for atrazine, and 3% of the samples exceeded the LOQs (0.001 to 0.5 µg/L). The overall relative risk of atrazine to impair surface water quality is ranked as moderate because the highest concentration detected (5.3 µg/L) was lower than the lowest EC50 value (22 µg/L) and the highest total monthly amounts of reported use were in May and June, when storm-related runoff is minimal. However, the toxicity of chlorpyrifos increased 7.9 fold when it was mixed with atrazine (Lydy and Linck, 2003). The major applications of atrazine are to Sudan grass (69%) and cornfields (15%). The relative risk for atrazine to contaminate sediments is "possible", based on its relatively moderate Koc value and its relatively long half-life in soils value.

Carbaryl is an insecticide that was reviewed for environmental fate (CDFG, 1998) and risk to aquatic organisms (DPR, 2003b). The Criteria Continuous Concentration (CCC) and the Criteria Maximum Concentration (CMC) values proposed by the CDFG for carbaryl in fresh water are both 2.53 µg/L. The reported amounts of carbaryl use showed a high total monthly amount of use in June suggesting that carbaryl may be present in irrigation runoff. Hundreds of surface water samples were analyzed for carbaryl (DPR, 2003b) and the maximum concentration detected (0.5 µg/L) is lower than the proposed CCC/CMC values and lower than the lowest 96-hour LC50 value (1.9 µg/L). Based on the relative toxicity ranking, the overall relative risk should be high, but because of the low concentrations observed in water samples, the fact that carbaryl is generally not applied during the winter storm season, and the decreased amounts of use from 1997 to 2001, the overall relative risk is moderate. There is a "possible" risk for carbaryl to contaminate sediments, as indicated by its relatively moderate Koc value and its relatively short half-life in soil value.

Copper oxide (ous; also known as cuprous oxide or copper (I) oxide) is a fungicide and an insecticide. The water solubility varies widely with pH and temperature variations, however copper oxide is almost insoluble (<2 ppb) in water at ambient temperature (25˚C). The lowest 96-hour LC50 was 69.7 µg/L tested on mysid (*Mysidopsis bahia*). The major applications of copper oxide are on peach and pear orchards. The total annual reported use amounts varied with the highest use in 1998 and lowest use in 2001. The total annual reported use amounts increased from 1994 to 1998 and then decreased from 1998 to 2001. The relatively high total monthly amounts of reported use were in January, April, and May. There are no Koc value data available for copper oxide. Since ionic (dissolved) copper is strongly adsorbed to soil particles, the relative risk for it to contaminate sediment is ranked as "potential".

Mancozeb is a fungicide and was ranked as posing a moderate relative risk to impair surface water quality because of the significant reduction in the total annual amounts of reported use in recent years, and because it has a low total monthly amounts of reported use during the winter storm season. However, as the major applications of mancozeb were to tomato fields in May, the relative risk to surface water quality depends on whether mancozeb occurs in the irrigation runoff. The lowest 96-hour LC50 value was 9.5 µg/L. The relative risk for mancozeb to contaminate sediments is “potential”, based on its relatively high Koc value.

Norflurazon is an herbicide. It was not selected in the initial list of target pesticides because of its low total amounts of reported use. DPR recommended that norflurazon be included on the list of target pesticides since it has been detected in surface water samples (Sanders, 2005). The 96-hour LC50 values, base on toxicity tests using aquatic animals, range from 3,800 to 16,300 µg/L. The EC50 values, based on toxicity testing using aquatic plants, are much lower and range from 13 to 86 µg/L. Almost two hundred surface water samples were collected from the Sacramento River watershed and analyzed for norflurazon. The highest observed concentration (0.98 µg/L) is much lower than the lowest toxicity value (EC50). The total annual amounts of reported norflurazon use decreased from 1992 to 1998, but in 1999 the amount of use increased. The total annual amounts reportedly used decreased again in 2000 and 2001. The highest use was in 1999 and the lowest use was in 1998. Winter storm runoff from agricultural fields could be a concern because the major applications were to orchards during the winter storm/dormant season (December to February) but the overall relative risk may be lower because of norflurazon’s moderate water solubility value. The relative risk for norflurazon to contaminate sediments is “possible”, based on its relatively moderate Koc value and its relatively long half-life in soil value.

Oryzalin is an herbicide that has a very low water solubility value and a moderate Koc value, so it tends to adsorb onto sediment. The 96-hour LC50 values range from 285 to 3,450 µg/L, based on toxicity testing using aquatic animals. The EC50 values, based on toxicity testing using aquatic plants, range from 15.4 to 72 µg/L. The major applications of oryzalin are on almond, prune, and walnut orchards during the storm season. The high total monthly amounts of reported oryzalin use were during the winter storm season, suggesting a relatively high risk for oryzalin to contaminate surface waters via agricultural runoff. However, oryzalin is almost insoluble in water and the reported surface water samples analytical data show that only 5 of 62 data values (DPR, 2003b) exceeded the LOQs (0.019 to 0.4 µg/L). The maximum concentration measured was 1.51 µg/L, which is well below the lowest toxicity (EC50) value. The overall relative risk for oryzalin to impair surface water quality may be decreasing because the total annual amounts of reported use decreased significantly in 2001. The relative risk for oryzalin to contaminate sediments is “possible”, based on its relatively moderate Koc value and its relatively low soil half-life value.

Phosmet is an insecticide and has been monitored in the Sacramento River watershed from 1992 to 2000 by various agencies, including the CVRWQCB. Over 600 surface water sample concentration data values are reported in the SWDB (DPR, 2003b), but none are over the LOQs (0.05 to 1.0 µg/L). The major applications of phosmet were on orchards (walnut, almond, and apple) during summer months. The highest total monthly amount of reported use was in July. The potential for phosmet to occur in orchard runoff during the winter storm season is low because the total monthly amounts reportedly used during the winter storm season months are low. Phosmet is ranked as posing a moderate overall relative risk to impair surface water quality because high concentrations have not been detected in surface water samples and because the major applications are not during the winter storm season. The relative risk for phosmet to contaminate sediments is "possible" because of its relatively moderate Koc value and its relatively low soil half-life value.

Simazine is an herbicide. It was not included on the initial list of target pesticides because of its relatively low total annual amount of reported use. DPR recommended that simazine be included on the target pesticide list because it has been detected in surface water samples (Sanders, 2005). The 96-hour LC50 values range from 4,300 to 1,000,000 µg/L, based on toxicity testing using aquatic animals. The EC50 values, based on toxicity testing using aquatic plants, range from 36 to 5,000 µg/L. Of the thousands of surface water sample concentration data values in the SWDB (DPR, 2003b), the highest concentration (6.1 µg/L) was lower than the lowest EC50 value. Therefore, the overall relative risk for simazine to impair surface water quality is ranked as moderate. The major applications of simazine were to walnut (50%) and almond (32%) orchards. The total annual amounts of reported simazine use have decreased slightly from 1992 to 2001. High total monthly amounts of simazine were reportedly used during the winter storm season (December to March). Although simazine may occur in storm runoff, the amount of simazine in the runoff may be low because its water solubility value is relatively low. Therefore, the overall relative risk to impair surface water quality is low. The relative risk for simazine to contaminate sediments is "possible"', based of its relatively moderate Koc value and its half-life in soil value.

The pesticides ranked as having relatively moderate toxicity are: 1,3-dichloropropene; 2,4-D, dimethylamine salt; bensulfuron methyl; copper sulfate (basic); copper sulfate (pentahydrate); cyprodinil; glyphosate-trimesium; MCPA, dimethylamine salt; metam-sodium; and propiconazole. All of these pesticides are relatively highly soluble in water, except for cyprodinil which is relatively moderately soluble in water. Among these pesticides, 1,3-dichloropropene, 2,4-D, dimethylamine salt, MCPA, dimethylamine salt, and metam-sodium have relatively low or very low Koc values and, therefore, are "unlikely to contaminate sediments.

1,3-dichloropropene is a fumigant and nematicide and its 96-hour LC50 values range from 640 to 7,090 µg/L. The total annual amounts of reported use increased from 1997 to 2001 and no amounts of use were reported before 1996 (DPR, 2003a). The major applications are to orchards (peach, prune, and walnut) in October and November. Although the application period is not strictly during the winter storm season (December to March), there is a risk for 1,3-dichloropropene to occur in agricultural runoff due to early storms. The relatively low Koc value for 1,3-dichloropropene and its relatively low half-life value indicate that it is "unlikely" to contaminate sediments.

2,4-D, dimethylamine salt is an herbicide that has been applied in great amounts, in terms of both weight and area. The total annual amounts of reported use increased from 1992 to 1997, decreased in 1998, and increased again from 1999 to 2001. The major applications were to rice fields in June and to wheat fields in February and March. The lowest 96-hour LC50 value was 140 µg/L, based on toxicity testing using grass shrimp. The lowest 120-hour EC50 value (51,200 µg/L), based on toxicity testing using aquatic plants, is much higher than the lowest 96-hour LC50. Therefore, the overall relative risk is based on the lower 96-hour LC50 value. There is a potential for 2,4-D, dimethylamine salt to occur in storm runoff from fields during the winter storm season. However, none of the 160 reported surface water sample measured concentrations (DPR, 2003b) exceeded the LOQs (0.1 and 1 µg/L). The relatively low Koc value and its relatively low half-life in soil value indicate that 2,4-D, dimethylamine salt is “unlikely” to contaminate sediments.

Bensulfuron methyl is an herbicide that is mainly used on rice fields. It has relatively moderate toxicity and relatively high water solubility values. The 96-hour LC50 values range from 71,000 to 270,000 µg/L, based on toxicity testing using aquatic animals. The EC50 value (800 µg/L) is based on toxicity testing using aquatic plants. The total annual amounts of reported use have significantly decreased in recent years. Since most of the reported total monthly amounts of reported bensulfuron methyl use are in May, the timing of water discharge from rice field plays a major role in its potential to impair surface water quality. Since bensulfuron methyl has a relatively moderate Koc value and a relatively low soil half-life value, the risk for it to contaminate sediment is “possible”.

Copper sulfate (basic) and copper sulfate (pentahydrate) are fungicides that have relatively high solubilities and are strongly adsorbed to soil particles (EXTOXNET database, 2003). The 96-hour LC50 values range from 200 to 1,788,000 µg/L for copper sulfate (basic) and from 130 to 28,000 µg/L for copper sulfate (pentahydrate), based on toxicity testing using rainbow trout (*Oncorhynchus mykiss*). The major applications of copper sulfate (basic) are to peach and pear orchards. The highest total monthly amount of reported use is in January. Therefore, there is a high relative risk for winter storm runoff to contain copper sulfate (basic). The major application (96%) of copper sulfate (pentahydrate) is to rice fields, with the highest total monthly amounts reportedly used in May. The total annual amounts of reported copper sulfate (pentahydrate) use increased in 2000 and 2001. Although no Koc values are available for copper sulfate (pentahydrate), ionic copper is strongly adsorbed to soil particles. Therefore, the relative risk for these two forms of copper sulfate to contaminate sediment is “potential”.

Cyprodinil is a fungicide that is moderately soluble to water. The 96-hour LC50 values are in range widely (433 to 8,140 µg/L). The lowest value was based on toxicity testing using eastern oysters (*Crassostrea virginica*). The total annual amount of reported cyprodinil use increased from 1998 to 2001, with the highest total annual amount used in 2000. The major applications of cyprodinil are to almond (62%) and prune (22%) orchards. The highest total monthly amounts reportedly used are in February and March (at the tail-end of the winter storm season). There are no water quality criteria or surface water sample concentration data available. The relative risk for cyprodinil to contaminate sediments is “potential”, based on its relatively high Koc value.

Glyphosate–trimesium is an herbicide. It is used almost year-round with relatively high uses reported between January and August (DPR, 2003a). The highest total monthly amount of glyphosate-trimesium reportedly used was in March. Generally, the glyphosate group of herbicides have relatively low toxicity to aquatic organisms. The 96-hour LC50 values range from 5,700 to 3,500,000 µg/L, based on toxicity testing using aquatic animals. The lowest toxicity value was based on toxicity testing using rainbow trout (*Oncorhynchus mykiss*). The range of EC50 values for glyphosate-trimesium, based on toxicity testing using aquatic plants, is from 170 to 122,000 µg/L, and the lowest 5-day EC50 value is 400 µg/L. The major applications are to almond, walnut, and prune orchards. The total annual amounts of reported glyphosate-trimesium use have increased since reporting of this chemical began in 1999. Glyphosate has a high propensity to adsorb onto soil particles, based of its high Koc value Therefore, the relative risk to sediment is "potential".

MCPA, dimethylamine salt (MCPA) is an herbicide. The 96-hour LC50 values, based on toxicity testing using aquatic animals, range from 42,000 to 306,000 µg/L. The EC50 values, based on toxicity testing using aquatic plants, range from 170 to 122,000 µg/L, and the lowest 120-hour EC50 value is 400 µg/L. MCPA is reportedly used in relatively high total annual amounts (DPR, 2003a). However, the reported total annual amounts used have decreased from 1998 to 2001. MCPA has a relatively high potential for contaminating surface water, based on its relatively high water solubility value and its relatively low Koc value. The peak period of application is in June, but relatively high amounts are also reportedly used in February, during the winter storm season. MCPA was detected in the Sacramento River watershed in February, March, June, and July. However, the concentrations (all below 2 µg/L) were much lower than the lowest toxicity level for aquatic organisms (400 µg/L). In addition, MCPA can be degraded to non-toxic levels in two weeks by aquatic microorganisms (USEPA, 1987, cited in EXTOXNET database). Therefore, the overall relative risk for MCPA to impair surface water quality may be lower than moderate. The relative risk for MCPA to contaminate sediments is "unlikely", based on its low Koc value.

Metam-sodium can be used as fumigant, fungicide, herbicide, microbiocide, and nematicide. The 96-hour LC50 values range from 510 to 34,100 µg/L, based on toxicity testing using fishes and crustaceans. The lowest LC50 value was based on toxicity testing using bluegill sunfish (*Lepomis macrochirus*). The total annual amounts of reported metam-sodium use varies by year, with the highest use reported in 1996 and lowest use reported in 2001. The total annual amount used in 2001 was 22% of total annual amount used in 1999 (DPR, 2003a). The major uses were to tomatoes (87%) in March and April. There is no metam-sodium concentration data available in the DPR SWDB database. Metam-sodium has very high water solubility (963,000 µg/L), so runoff containing metam-sodium may pose a relatively high risk to surface water. The relative risk to sediment contamination is unlikely because of its relatively very low Koc value and its relatively very low half-life in soil value.

Propiconazole is a fungicide that has high water solubility. The 96-hour toxicity ranges from 510 to 49,000 µg/L with the lowest toxicity value based on toxicity testing using a mysid (*Mysidopsis bahia).* Between 1997 and 2001, the highest total annual amount of reported use was in 1998 and the lowest total annual amount of reported use was in 2001. In 2001, the total annual amount of reported propiconazole use had decreased to 5% of the peak total annual amount of use reported in 1998. The high uses are to almond (57%), prune (30%), and peach (2%) orchards in February and March (at the end of the winter storm season). The relative risk for propiconazole to contaminate sediments is "possible", based of its relatively moderate Koc value and its relatively high half-life in soil value.

4.3. "Low" Overall Relative Risk Pesticides

Eight target pesticides are ranked as having low overall relative risk to impair surface water quality (Table 5C). Three of these pesticides – glyphosate, isopropylamine salt, methyl bromide, and triclopyr, triethylamine salt - have very high water solubility values (ranging from 13,400 to 3,310,000 mg/L). The other five target pesticides (having low overall relative risks) have a variety of water solubility values : EPTC has a relatively high water solubility value, azoxystrobin and iprodione have relatively moderate water solubility values, triforine has a relatively low water solubility value, and copper oxychloride sulfate has no associated water solubility values reported and it has been reported to be insoluble in water.

Of the eight pesticides ranked as posing low overall relative risks to impair surface water quality, the total annual amounts of reported use of four pesticides (in terms of weight and area of use), copper oxychloride sulfate, EPTC, iprodione, and triforine have decreased significantly between 1998 and 2001. In addition, the use of methyl bromide was phased-out by USEPA in 2000. The overall relative risk for glyphosate to contaminate surface water may be higher than otherwise expected because it is more toxic to aquatic plants than to aquatic animals.

Glyphosate, isopropylamine salt is an herbicide. Relatively high total monthly amounts of reported use were reported in February, March and July. Generally, the glyphosate group of herbicides has relatively low toxicity values for aquatic organisms. The 96-hour LC50 values range from 1,300 to 1,000,000 µg/L. The lowest toxicity value is based on toxicity testing using rainbow trout (*Oncorhynchus mykiss*). The EC50 values for glyphosate, isopropylamine salt, based on toxicity testing using aquatic plants, range from 770 to 38,600 µg/L, and the 120-hour EC50 value is 11,750 µg/L. The major applications are to almond, walnut, and prune orchards. The total annual amounts of reported use have generally increased. Glyphosate has a high propensity to adsorb onto soil particles, based on its relatively high Koc value. Therefore, the relative risk for it to contaminate sediments is "potential".

Methyl bromide is a gaseous fungicide that is reportedly used in relatively high amounts on orchards during the fall (DPR, 2003a). There are no 96-hour LC50 values available for methyl bromide and it has only one associated 48-hour EC50 value (2,600 µg/L), based on toxicity testing using the water flea (*Daphnia magna*). Since the major application months are in October and November, the potential for methyl bromide to be present in winter storm runoff is low. The total annual amounts reportedly used have decreased significantly since the USEPA-scheduled phase-out of methyl bromide use by 2000. The relative risk for methyl bromide to contaminate sediments is “unlikely”, based on its relatively low Koc value.

Triclopyr, triethylamine salt is an herbicide. The 96-hour LC50 values range from 58,000 to 1,000,000 µg/L, based on toxicity testing using aquatic animals. For aquatic plants, the EC50 values range from 5,900 to 39,100 µg/L, with the lowest 120-hour EC50 value of 14,900 µg/L. The major use of triclopyr is to rice fields in June and July. The total annual amounts of reported use increased from 1998 to 2000 and decreased slightly in 2001. Runoff from rice fields may be a concern based on trichlopyr’s relatively high water solubility value. The relative risk for triclopyr to contaminate sediments is “unlikely”, based on its relatively low Koc value and its moderate soil half-life value.

EPTC is an herbicide. The 96-hour LC50 ranges from 11,500 to 180,000 µg/L, based on toxicity testing using aquatic animals. The EC50 values, based on toxicity testing using aquatic plants, range from 1,400 to 41,000 µg/L, with the lowest 96-hour EC50 value of 1,400 µg/L. Over 500 surface water sample concentrations were measured in the Sacramento River watershed (DPR, 2003b). The highest concentration (0.716 µg/L) is much lower than the lowest EC50 value. The total annual amounts of reported EPTC use has decreased significantly in recent years. In 2001, the amount of use was only 17% of the total annual amount reportedly used in 1993. Because of the decreased total annual amounts of reported use, EPTC was not included on the list of the top 30 highest-use pesticides from 1998 to 2001. The relative risk for EPTC to contaminate sediments is “possible”, based on its Koc value.

Azoxystrobin is a fungicide. It is moderately soluble in water (10 mg/L). The 96-hour LC50 ranges from 56,000 to 1,100,000 µg/L. The lowest LC50 value is based on toxicity testing using a mysid (*Mysidopsis bahia*). The use of azoxystrobin was reported beginning in 1997 with increasing use in recent years. The lowest total annual amount of reported use was in 1997 and the highest total annual amount of reported use, in 2000, was about 40 times greater (DPR, 2003a). The highest total monthly amounts of reported uses were in July and August. The major applications of azoxystrobin are to rice fields (39%), almond orchards (34%), and tomato fields (15%). The relative risk for azoxystrobin to contaminate sediments is “possible”, based on its relatively moderate Koc value and its relatively large soil half-life value.

Iprodione is a fungicide that is slightly toxic to aquatic organisms. The 96-hour LC50 values for iprodione range from 2,300 to 7,800 µg/L (USEPA, 2003). Iprodione is ranked as posing a low overall relative risk to impair surface water quality because of its relatively low toxicity to aquatic organisms. In addition, the total annual amounts of reported use have decreased significantly in recent years. In 2001, the total annual amount reportedly used was 15% of the total annual amount reportedly used in 1995 (the highest use year). Iprodione is not included on the list of top the 30 highest-use pesticides from 1998 to 2001. However, runoff from fields is a concern because the major total monthly amounts of reported agricultural uses of iprodione to orchards occur during the winter storm season (January and February) and iprodione has a relatively moderate solubility value . The relative risk for iprodione to contaminate sediments is "possible", based on its relatively moderate Koc value and its relatively low soil half-life value.

Triforine is a fungicide that is slightly soluble in water. There are no 96-hour LC50 values reported in the EPA toxicity database, and the 48-hour EC50 values range from 21,400 to 1,000,000 µg/L. The lowest 48-hour EC50 value (221,400 µg/L) is based on toxicity testing using rainbow trout (*Oncorhynchus mykiss*). There may be a risk for triforine to enter surface waters via agricultural runoff during the winter storm season because the major applications are to orchards (peach and prune) in March (at the end of the winter storm season). However, the amount of triforine used has decreased significantly. The highest use (31,823 lbs) was in 1993 and the lowest use (only 1 lb) was in 2000. Triforine was not included on the list of top 30 highest-use pesticides from 1998 to 2001. Triforine is ranked as posing a low overall relative risk to impair surface water based on its relatively low toxicity values and its relatively low solubility values. The relative risk for triforine to contaminate sediments is "possible", based on its relatively moderate Koc value.

Copper oxychloride sulfate can be used as a fungicide and as an insecticide. Copper oxychloride sulfate is almost insoluble in water. Copper oxychloride sulfate was ranked as having a low overall risk to impair surface water quality because of its low toxicity value. The total annual amounts of reported use of copper oxychloride sulfate decreased from 1992 to 2001. The major applications were to peach and pear orchards. The relatively high total monthly amounts of reported use were between January and March with the highest total monthly amount of reported use in January (i.e., during the winter storm season). Although no Koc or soil half-life values are available, ionic copper is strongly adsorbed to soil particles, so the relative risk for copper oxychloride sulfate to contaminate sediment is "potential".

5. Summary and Conclusions

Over three hundred pesticides are reportedly used for agricultural purposes in the Sacramento River watershed. Seventy-one pesticides were initially selected for relative risk evaluation based on the amounts (by weight and/or area) of reported use (Table 1). The 71 pesticides account for at least 90% of the total reported agricultural pesticides usage in terms of weight, and for 60% of the usage in terms of acreage for the Sacramento Valley. After removal from the initial list of those pesticides that were determined to have relatively very low toxicity to aquatic organisms (such as sulfur and cottonseed oil), and then adding four pesticides (e.g. atrazine) that were recommended by DPR because they have been detected in surface water samples collected in the Sacramento River watershed (Sanders, 2005), a total of 48 target pesticides were identified (Table 2). These 48 target pesticides were evaluated and ranked as posing high, moderate, or low overall relative risk to impair surface water quality. Of the 48 target pesticides evaluated, 22 are ranked as posing high overall relative risk, 18 are ranked as posing moderate overall relative risk, and eight are ranked as posing low overall relative risk to impair surface water quality.

The evaluation of the overall relative risk ranks were mainly based on the lowest acute toxicity value for the most sensitive aquatic organism species, the maximum concentrations of the pesticides in surface water samples collected from the Sacramento River watershed, the potential for the pesticides to occur in agricultural runoff (with the winter storm season being a critical period for generating significant runoff), and the trends in total annual and monthly amounts of reported use (DPR, 2003a). Toxicity values played a critical role in the overall relative risk evaluation process . The overall relative risk evaluations also considered the potential relative risks for the pesticides to contaminate sediment. However, the overall relative risk rank was modified for some pesticides when the trends of total annual amounts of reported use were considered (e.g.if the trend of total annual amounts of reported use increased during the ten-year period [from 1992 to 2001]), the overall relative risk might have been increased one relative risk rank.

Of the 22 pesticides evaluated as having high overall relative risk to impair surface water quality, three were not reviewed by the DPR, the CDFG, or the CVRWQCB. These three pesticides (lambda cyhalothrin, oxyfluorfen, and trifluralin) are highly toxic to aquatic organisms and have relatively very low water solubility values. Among the 22 pesticides, seven, including diazinon and chlorpyrifos, are included on the 303(d) list for waterways in the Sacramento River watershed and are highly, to very highly, toxic to aquatic organisms. Among the pesticides evaluated as posing high overall relative riskto impair surface water quality, three are pyrethroids. Although pyrethroid pesticides are difficult to detect in surface water, their potential for impairing surface water (primarily by being toxic to aquatic organisms) or for contaminating sediments (due to pesticide adsorbtion to the sediments) should be considered.

Based on the information derived from the PUR database, the total annual amounts of reported use for 17 of the 22 pesticides has decreased by at least 23% from the highest usage amounts, and the total annual amounts of reported use of some pesticides (such as carbofuran and methidathion) have decreased even more (over 90% reduction). From 1998 to 2001, five pesticides -: azinphos methyl, carbofuran, malathion, methidathion, and methyl parathion - were not included on the list of the top 30 highest-use pesticides. Therefore, their overall relative risks may be lower than presented here. In contrast, the total annual amounts of reported use of some pesticides - esfenvalerate, lambda cyhalothrin, and propanil - have increased by over 90% from 1998 to 2001. Their overall relative risks to impair surface water quality may need to be further evaluated.

The overall relative risk was not evaluated for most combinations of pesticides applied at the same time, except for molinate and thiobencarb which are commonly used in combination. The overall relative risks of combinations of pesticides could be higher than the overall relative risks of the individual pesticides (due to additive or synergistic effects).

The evaluation of 18 pesticides as posing moderate overall relative risks to impair surface water quality is based primarily on their toxicities to aquatic organisms. But the overall relative risk was also evaluated considering other factors such as available concentration data, season (months) of reported use, and trends of total annual amounts of reported use. Eight of these pesticides -: atrazine, carbaryl, copper oxide (ous), mancozeb, norflurazon, oryzalin, phosmet, and simazine - are highly toxic to aquatic organisms but are ranked as posing only moderate overall relative risks to impair surface water quality, based on the consideration of these other factors. The other ten pesticides evaluated as posing moderate overall risks to impair surface water quality are moderately to slightly toxic to aquatic organisms, so their overall relative risks are ranked as moderate. In terms of their total annual amounts of reported use (based on weight), 1,3-dichloropropene, atrazine, cyprodinil, glyphosate-trimesium, and the two copper sulfate fungicides have increased from 1998 to 2001. Three pesticides - (atrazine, norflurazon, and simazine -) are included in the target pesticides list and were evaluated for their overall relative risks to impair surface water quality, based on the recommendation of DPR who noted that they have been detected in surface water samples collected from the Sacramento River watershed (Sanders, 2005. Atrazine is known to increase the toxicity of some other pesticides (e.g. chlorpyrifos). Norflurazon and simazine were detected in surface water samples collected from the Sacramento River watershed, but the maximum concentrations were far below their respective lowest 96-hour LC50 values and were also below their respective lowest EC50 values.

The eight pesticides ranked as having low overall relative risk are only slightly toxic to aquatic organisms. However, there may be a higher overall relative risk to impair surface water quality for some of these pesticides, particularly the pesticides with increased total annual amounts of reported use from 1998 to 2001 (e.g. azoxystrobin, glyphosate-isopropylamine salt, and triclopyr-triethylamine salt). There are four pesticides - copper oxychloride sulfate, EPTC, iprodione, and triforine - ranked as posing low overall relative risks to impair surface water quality that were not included on the list of top 30 highest-use pesticides from 1998 to 2001.

The overall relative risks were evaluated and ranked using the lowest toxicity values as a major deciding factor. The lowest toxicity values are 96-hour or /48-hour LC50 or EC50 values, or 120-hour or 96-hour EC50 values (only one pesticide value was based on toxicity testing for a 128-hour period). Of 17 herbicides, 15 had lower toxicity values for aquatic plants than for aquatic animals, but the overall relative risks of only eight of them were modified when their relative toxicity values for aquatic plants were included in the evaluation. The overall relative risk ranks of three herbicides - diuron, paraquat dichloride, and propanil - were modified from moderate to high, and the overall relative risks ranks of six herbicides - atrazine, bensulfuron methyl, glyphosate-trimesium, MCPA, norflurazon, and simazine - were modified from low to moderate based on special considerations discussed for each pesticide, above.

Environmental conditions, such as seasonal weather patterns, are critical in evaluating the potential overall relative risks for pesticides to impair surface water quality. For the purposes of this evaluation, the major climate consideration was the winter storm season (December to March), during which significant agricultural runoff (potentially containing pesticides) is most likely to occur.

6. Future work

Further evaluation of the overall relative risks to aquatic organisms from pesticides in surface water and adsorbed to sediment in the Sacramento River watershed should focus on the pesticides ranked as having high and moderate overall relative risks. The pesticides ranked as posing high overall relative risks and having high Koc values need to be studied in more detail to evaluate their potential relative risks to adsorbed to (contaminate) sediments. Additional evaluation of runoff potential from irrigated lands will help refine the overall relative risk ranking of pesticides applied during the irrigation season. The evaluations should include the total annual amounts of reported pesticide use in more recent years, the types of pesticide application methods, and the runoff potential from different types of fields and crops.

References

ARS (Agricultural Research Service). 2003. USDA ACSL. The ARS Pesticides Properties Database. Available: http://www.arsusda.gov/acsl/services/ppdb/

CDFG (California Department of Fish and Game). 2003. Surface Water Hazard Assessments to Aquatic Organisms reports. Available: www.cdpr.ca.gov/docs/sw/hazasm.htm

CDFG. 1998. *Hazard Assessment of the Insecticide Carbaryl to Aquatic Life in the Sacramento-San Joaquin River System.* Admin report, 98-1.

DPR (Department of Pesticide Regulation). 2003a. Pesticide use reporting (PUR) database. Available: http://www.cdpr.ca.gov/docs/pur/purmain.htm

DPR. 2003b. Surface water database (SWDB). Available: http://www.cdpr.ca.gov/docs/sw/surfdata.htm

DPR. 2003c. Preliminary results of study #214: monitoring the occurrence and concentration of esfenvalerate and permethrin pyrethroids.

DPR. 2004a. Surface Water Protocols. Available: www.cdpr.ca.gov/docs/sw/protocol.htm

DPR. 2004b. Fate review by Department of Pesticide Regulation. Available: http://www.cdpr.ca.gov/docs//empm/pubs/envfate.htm

EXTOXNET. 2003. Pesticides information by Extension Toxicology Network. Available: http://pmep.cce.cornell.edu/profiles/extoxnet/

Holmes, R., V. D. Vlaming, and C. Foe. 2000. *Sources and concentrations of diazinon in the Sacramento watershed during the 1994 orchard dormant spray season.* CVRWQCB. Sacramento, CA.

Karkoski, J. 2003. *Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Orchard Pesticide Runoff and Diazinon Runoff into the Sacramento and Feather Rivers, Final Staff Report.* CVRWQCB.

Kuivila, K.M. and C. Foe. 1995. Concentrations, transport and biological effects of dormant pesticides in the Sac Francisco estuary, California. *Env. Toxic. and Chemi.* Vol.14. No. 7. 1141-1150.

Kuivila, K.M. and D. Weston, I. Werner, W. Jennings, and K. Eder. 2004. *Assessment of pesticides effects on fish and the food resources in the Sacramento-San Joaquin Delta.* (Unpublished).

Lydy, M.J. and S.L. Link. 2003. Assessing the impact of triazine herbicides on organophosphate insecticides toxicity to the earthworm *Eisenia fetida*. *Environ. Contam. Toxicol.* 45. 343-349.

Nordmark, C.E., K.P. Bennet, H. Feng, J. Hernandez, and P. Lee. 1998. Occurrence of aquatic toxicity and dormant-spray pesticides detection in the Sacramento River watershed, Winter 1996-97. California EPA, Department of Pesticides Regulation, Environmental hazard assessment program. EH98-01. February 1998.

OSU (Oregon State University). 1994. OSU Extension Pesticides Properties Database. Available: http://npic.orst.edu/ppdmove.htm

Sanders, J.S. 2005. Comments on Relative Risk Evaluation for Pesticides Used in the Sacramento River Watershed. Memorandum prepared for Joe Karkoski (CVRWQCB) by John S. Sanders (Chief, Environmental Management Branch), Department of Pesticide Regulation. February 24, 2005. Sacramento, CA

SWRCB (State Water Resource Control Board). 2003. The Section 303(d) List of Water Quality Limited Segments. Available: http://www.swrcb.ca.gov/tmdl/303d_list.html

SWRCB. 1984. *Rice herbicides: molinate and thiobencarb*. Special projects report No. 84-4sp. April 1984.

SWRCB. 1990. Sacramento River Toxic Chemical Risk Assessment project. 90-11WQ. October 1990.

USEPA (United States of Environmental Protection Agency). 1976. Water Quality Criteria. (The RED book) Washington DC. http://www.epa.gov/waterscience/criteria/aqlife.html#final

USEPA. 1987. Health advisory. Office of Drinking Water. [NEED SOURCE INFO]

USEPA, 2003. Ecological Effects Branch Pesticide EcoToxicity Database. Available: http://www.epa.gov/oppefed1/general/databasesdescription.htm#efd

Figure 1. Flow chart of the relative risk evaluation process

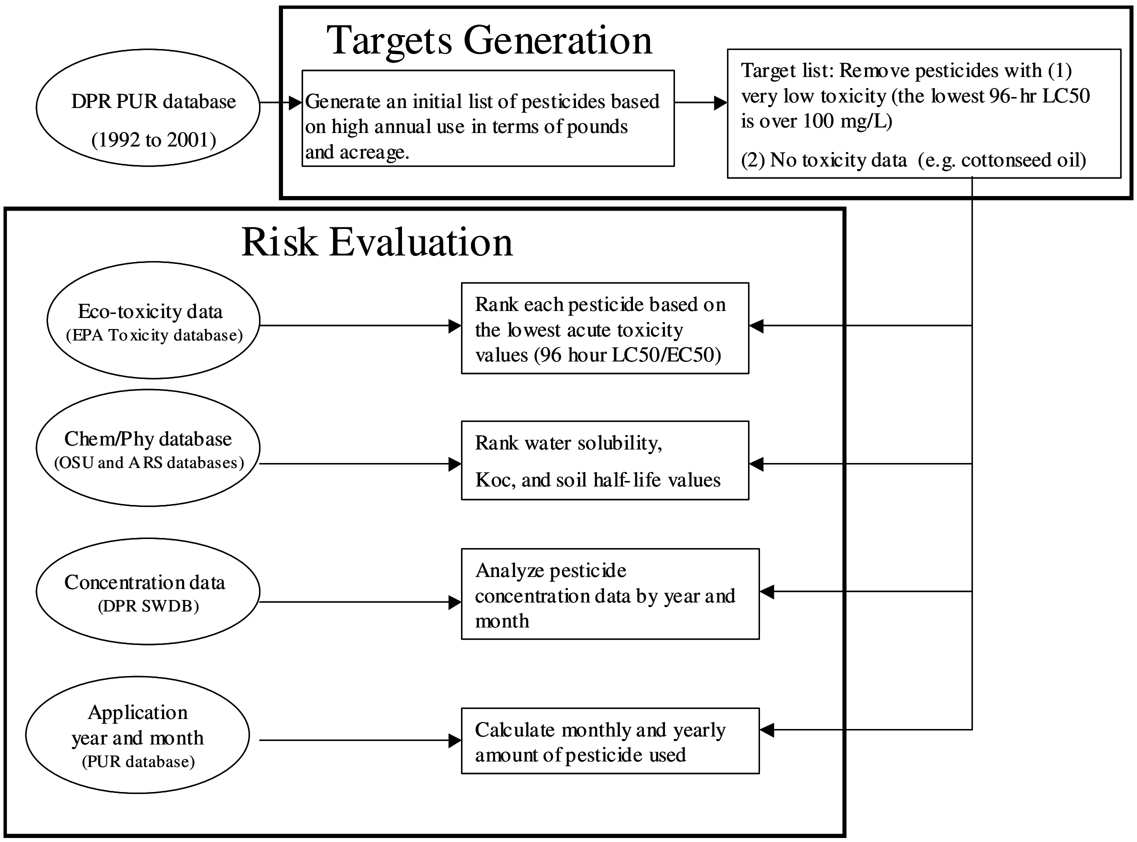


Figure 2. Flow chart of overall relative risk rank evaluation.

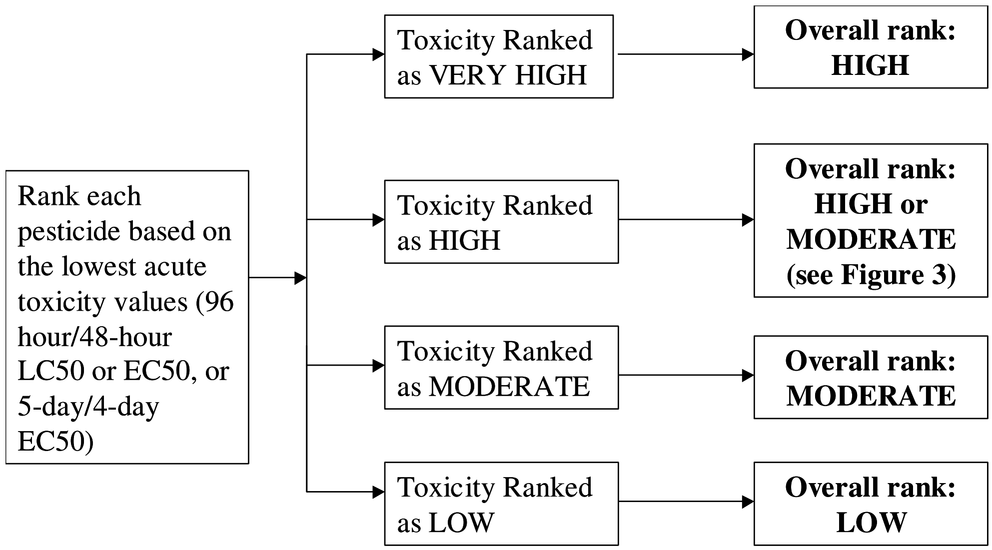


Figure 3. Flow chart of overall relative risk evaluation for the pesticides with high or moderate toxicity relative risk ranks.

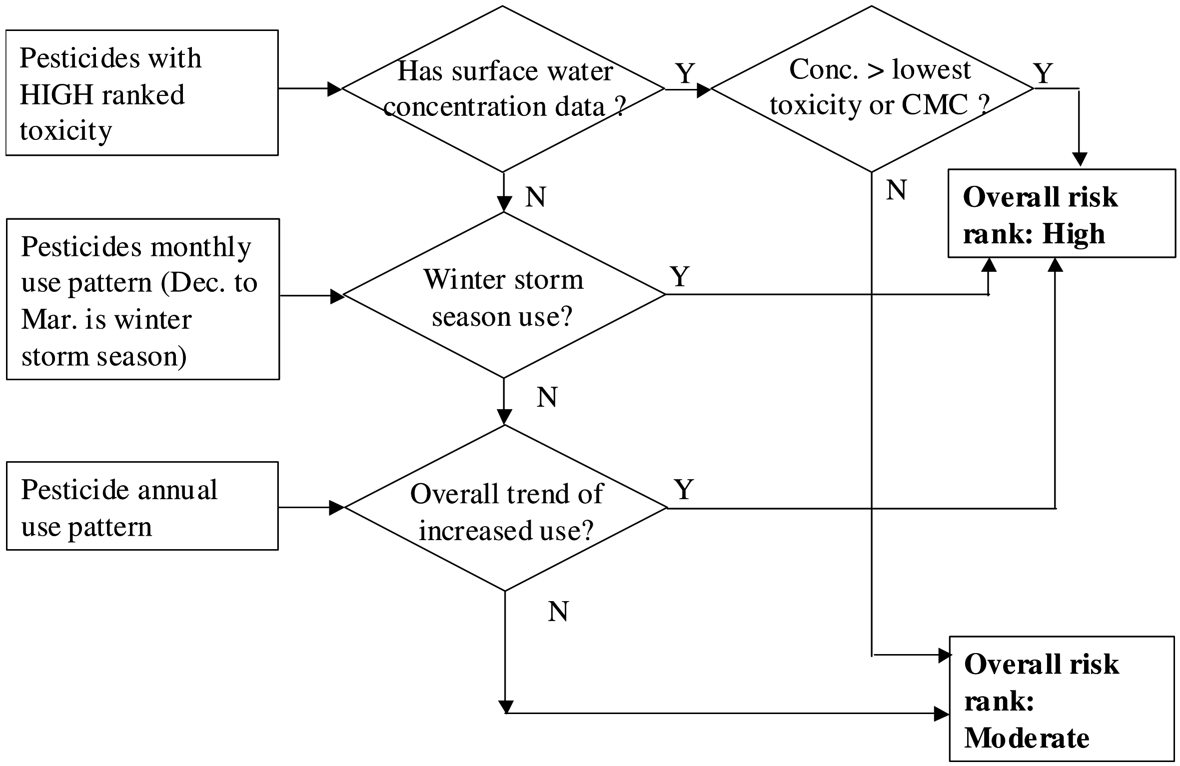


Table 1. Initial pesticide list.

CHEMCODE	Active Ingredient Chemical Name	Reason for removal*	Number of years in top 30
573	1,3-DICHLOROPROPENE		4
806	2,4-D, DIMETHYLAMINE SALT		10
1363	AMMONIUM SULFATE	3	2
314	AZINPHOS METHYL		6
4037	AZOXYSTROBIN		3
2263	BENSULFURON METHYL		10
104	CAPTAN		10
105	CARBARYL		6
106	CARBOFURAN		6
136	CHLOROPICRIN	2	8
677	CHLOROTHALONIL		8
253	CHLORPYRIFOS		10
142	CITRIC ACID	2	2
3550	COPPER AMMONIUM COMPLEX	3	1
151	COPPER HYDROXIDE	3	10
175	COPPER OXIDE (OUS)		2
158	COPPER OXYCHLORIDE SULFATE		1
162	COPPER SULFATE (BASIC)		10
161	COPPER SULFATE (PENTAHYDRATE)		10
1015	COTTONSEED OIL	2	1
4000	CYPRODINIL		2
198	DIAZINON		10
1861	DIMETHYL POLY SILOXANE	3	8
264	EPTC		1
2321	ESFENVALERATE		8
1855	GLYPHOSATE, ISOPROPYLAMINE SALT		10
2327	GLYPHOSATE-TRIMESIUM		1
2081	IPRODIONE		4
342	ISOPROPYL ALCOHOL	3	10
2297	LAMBDA CYHALOTHRIN		3
367	MALATHION		2
211	MANCOZEB		1
369	MANEB		8
2045	MCIAL CODE 401	1	6
786	MCPA, DIMETHYLAMINE SALT		9
616	METAM-SODIUM		9
1689	METHIDATHION		6
385	METHYL BROMIDE		10
394	METHYL PARATHION		2
3519	METHYL SOYATE	3	1
401	MINERAL OIL	1	10
449	MOLINATE		10
2073	NONYL PHENOXY HYDROXYPOLY (OXYETHYLENE)	3	2
1743	NONYL PHENOXY POLY (ETHYLENE OXY) ETHANOL	3	8
1244	OCTYL PHENOXY POLY ETHOXY ETHANOL	3	10

* 1 adjuvant; 2 very low toxicity; 3 no toxicity data

Table 1. Initial pesticide list (continued).

CHEMCODE	Active Ingredient Chemical Name	Reason for removal*	Number of years in top 30
1156	OLEIC ACID	3	9
2266	OLEIC ACID, METHYL ESTER	3	2
1868	ORYZALIN		6
1973	OXYFLUORFEN		10
1601	PARAQUAT DICHLORIDE		3
2008	PERMETHRIN		7
2106	PETROLEUM DISTILLATES, REFINED	1	2
473	PETROLEUM HYDROCARBONS	1	6
765	PETROLEUM OIL, UNCLASSIFIED	1	10
335	PHOSMET		5
871	PHOSPHORIC ACID	3	10
2111	POLYACRYLAMIDE POLYMER	1	7
1314	POLY-I-PARA-MENTHENE	1	9
1444	POLYOXYETHYLENE MIXED FATTY ACID ESTER	1	4
503	PROPANIL		5
445	PROPARGITE		9
2276	PROPICONAZOLE		3
507	PROPYLENE GLYCOL	1	4
536	SODIUM CHLORATE	2	2
560	SULFUR	2	10
1933	THIOBENCARB		10
2131	TRICLOPYR, TRIETHYLAMINE SALT		4
597	TRIFLURALIN		10
1905	TRIFORINE		2
1231	VEGETABLE OIL	2	1
629	ZIRAM		10

* 1 adjuvant; 2 very low toxicity; 3 no toxicity data

Table 2. Target pesticide list.

CHEMCODE	Active Ingredient Chemical Name	Number of years in top 30	High use between 1998 and 2001*
573	1,3-DICHLOROPROPENE	4	y
806	2,4-D, DIMETHYLAMINE SALT	10	y
314	AZINPHOS METHYL	6	n
4037	AZOXYSTROBIN	3	y
2263	BENSULFURON METHYL	10	y
104	CAPTAN	10	y
105	CARBARYL	6	y
106	CARBOFURAN	6	n
677	CHLOROTHALONIL	8	y
253	CHLORPYRIFOS	10	y
175	COPPER OXIDE (OUS)	2	y
158	COPPER OXYCHLORIDE SULFATE	1	n
162	COPPER SULFATE (BASIC)	10	y
161	COPPER SULFATE (PENTAHYDRATE)	10	y
4000	CYPRODINIL	2	y
198	DIAZINON	10	y
264	EPTC	1	n
2321	ESFENVALERATE	8	y
1855	GLYPHOSATE, ISOPROPYLAMINE SALT	10	y
2327	GLYPHOSATE-TRIMESIUM	1	y
2081	IPRODIONE	4	n
2297	LAMBDA CYHALOTHRIN	3	y
367	MALATHION	2	n
211	MANCOZEB	1	y
369	MANEB	8	y
616	METAM-SODIUM	9	y
786	MCPA, DIMETHYLAMINE SALT	9	y
1689	METHIDATHION	6	n
385	METHYL BROMIDE	10	y
394	METHYL PARATHION	2	n
449	MOLINATE	10	y
1868	ORYZALIN	6	y
1973	OXYFLUORFEN	10	y
1601	PARAQUAT DICHLORIDE	3	y
2008	PERMETHRIN	7	y
335	PHOSMET	5	y
503	PROPANIL	5	y
445	PROPARGITE	9	y
2276	PROPICONAZOLE	3	y
1933	THIOBENCARB	10	y
2131	TRICLOPYR, TRIETHYLAMINE SALT	4	y
597	TRIFLURALIN	10	y
1905	TRIFORINE	2	n
629	ZIRAM	10	y
45	Atrazine**	0	n
231	Diuron**	0	n
2019	Norflurazon**	0	n
531	Simazine**	0	n

* Pesticide was in top 30 high annual uses between 1998 and 2001 (4-year list)
**pesticides were not selected in Table 1 but DPR staff recommended pesticides to be added to the list

Table 3. Criteria for relative risk ranking, by parameter.

	Ranking				
Parameter	**Very high**	**High**	**Moderate**	**Low**	**Very low**
Toxicity (96 hour LC50 or EC50)	<1 µg/L	1 to 99 µg/L	100 µg/L to 999 µg/L	1 mg/L to 99 mg/L	>100 mg/L
Log(water solubility (mg/L))	> 3	2.001 to 3	1 to 2	≥0 and <1	<0 (water solubility less than 10)
Koc	>10,000	1,000 to 9,999	100 to 999	10 to 99	<10
Half-life in soils (day)	>1,000	101 to 1,000	31 to 100	10 to 30	<10

Table 4. Toxicity values for selected herbicides.

CHEM NAME	RISK RANK	LOWEST VALUE (ug/L)	TEST TIME (hr)	TIME RANGE	TOXICITY (ug/L)	COMMON NAME	TAXONOMIC
2,4-D Dimethylamine salt	low	51,200	120	5 to 14 D	580 to188,500	Green algae	Selenastrum capricornutum
Atrazine	high	22	120	2 hr to 14 D	22 to 460	Algae	Isochrysis galbana
Bensulfuron Methyl	moderate	800	128	128 hr	800	Green algae	Selenastrum capricornutum
Diuron	high	2.4	96	4 to 10 D	2.4 to 95	Green algae	Selenastrum capricornutum
EPTC	low	1,400	96	4 to 5 D	1,400 to 41,000	Green algae	Selenastrum capricornutum
Glyphosate	low	11,750	96	4 to 14 D	770 to 38,600	Bluegreen algae	Anabaena flos-aquae
Glyphosate-trimesium	moderate	700	120	5 to14 D	700 to 33,400	Duckweed	Lemna gibba
MCPA Dimethylamine salt	moderate	400	120	5 to 14 D	170 to 122,000	Bluegreen algae	Anabaena flos-aquae
Molinate	moderate	220	96	4 to 14 D	220 to 21,100	Green algae	Selenastrum capricornutum
Norflurazon	high	13	120	5 to 14 D	13 to 86	Green algae	Kirchneria subcapitata
Oryzalin	high	15.4	120	5 D	15.4 to 72	Duckweed	Lemna gibba
Oxyfluorfen	very high	0.29	96	4 to 10 D	0.29 to 2.9	Green algae	Selenastrum capricornutum
Paraquat dichloride	very high	0.55	96	4 to 14 D	0.55 to 50,000	Freshwater diatom	Navicula pelliculosa
Propanil	high	16	120	5 to 14 D	16 to 110	Freshwater diatom	Navicula pelliculosa
Simazine	high	36	120	5 to 14 D	36 to 5,000	Bluegreen algae	Anabaena flos-aquae
Thiobencarb	high	17	120	4 to 14 D	17 to 3,100	Green algae	Selenastrum capricornutum
Triclopyr, triethylamine salt	low	14,900	120	4 to 14 D	5,900 to 39,100	Marine diatom	Skeletonema costatum
Trifluralin	high	15.3	120	5 to 14 D	15.3 to 5000	Freshwater diatom	Navicula pelliculosa

Tables 5A through 5C. Ranking of overall relative risk for target pesticides (pesticides in the shaded areas do not occur among the top 30 pesticides in terms of highest use (by pounds applied or by acreages applied to, from1998 to 2001; N/A means no data available).

Table 5A. High overall relative risk pesticides.

Chem Name	Overall Rank	Rank of toxicity	Rank of solubility	Rank of Koc	Rank of soil half-life	Lowest Toxicity (ug/L)	Water Solubility (mg/l)	Sorption Coefficient (soil Koc)	Soil Half-life (days)	Log (solubility)	Sedment contamination risk
AZINPHOS METHYL	high	very high	moderate	high	low	0.1	29	1000	10	1.46	potential
CAPTAN	high	high	low	moderate	very low	16.2	5.1	200	2.5	0.71	possible
CARBOFURAN	high	high	high	low	moderate	7.3	351	22	50	2.55	unlikely
CHLOROTHALONIL	high	high	very low	high	low	26	0.6	1380	30	-0.22	potential
CHLORPYRIFOS	high	very high	very low	high	low	0.035	0.4	6070	30	-0.40	potential
DIAZINON	high	very high	moderate	high	moderate	0.2	60	1000	40	1.78	potential
DIURON	high	high	moderate	moderate	moderate	2.4	42	477	90	1.62	possible
ESFENVALERATE	high	very high	very low	high	moderate	0.07	0.0002	5273	35	-3.70	potential
LAMBDA CYHALOTHRIN	high	very high	very low	very high	low	0.0041	0.005	180,000	30	-2.30	potential
MALATHION	high	very high	high	high	very low	0.5	130	1800	1	2.11	potential
MANEB	high	high	low	moderate	low	33	6	240	30	0.78	possible
METHIDATHION	high	very high	high	moderate	very low	0.7	220	400	7	2.34	possible
METHYL PARATHION	high	very high	moderate	high	very low	0.78	60	5100	5	1.78	potential
MOLINATE	high	high	high	moderate	low	13	970	190	21	2.99	possible
OXYFLUORFEN	high	very high	very low	very high	moderate	0.29	0.1	100,000	35	-1.00	potential
PARAQUAT DICHLORIDE	high	very high	very high	very high	high	0.55	626,000	10,000	620	5.80	potential
PERMETHRIN	high	very high	very low	very high	low	0.018	0.006	100,000	30	-2.22	potential
PROPANIL	high	high	high	moderate	very low	16	200	149	1	2.30	possible
PROPARGITE	high	high	very low	high	moderate	31	0.5	4000	56	-0.30	potential
THIOBENCARB	high	high	moderate	moderate	low	3.1	28	900	21	1.45	possible
TRIFLURALIN	high	high	very low	high	moderate	8.4	0.3	8000	60	-0.52	potential
ZIRAM	high	high	moderate	moderate	low	8	65	400	30	1.81	possible

Table 5B. Moderate overall relative risk pesticides.

Chem Name	Overall Rank	Rank of toxicity	Rank of solubility	Rank of Koc	Rank of soil half-life	Lowest Toxicity (ug/L)	Water Solubility (mg/l)	Sorption Coefficient (soil Koc)	Soil Half-life (days)	Log(solubility)	Sedment contamination risk
1,3-DICHLOROPROPENE	moderate	moderate	very high	low	low	640	2,250	32	10	3.35	unlikely
2,4-D, DIMETHYLAMINE SALT	moderate	moderate	very high	low	low	140	796,000	20	10	1.00	unlikely
ATRAZINE	moderate	high	moderate	moderate	high	22	33	147	173	1.52	possible
BENSULFURON METHYL	moderate	moderate	high	moderate	very low	800	120	370	5	2.08	possible
CARBARYL	moderate	high	high	moderate	low	1.9	120	300	10	2.08	possible
COPPER OXIDE (OUS)	moderate	high	very low	high	N/A	69.7	0.002	N/A	N/A	-2.70	potential
COPPER SULFATE (BASIC)	moderate	moderate	very high	high	N/A	200	2,305	N/A	N/A	3.36	potential
COPPER SULFATE (PENTAHYDRATE)	moderate	moderate	very high	high	N/A	130	2,305	N/A	N/A	3.36	potential
CYPRODINIL	moderate	moderate	moderate	high	high	443	16	1,470	126	1.20	potential
GLYPHOSATE-TRIMESIUM	moderate	moderate	very high	very high	very low	700	3,310,000	24,750	6	2.08	potential
MANCOZEB	moderate	high	low	high	moderate	9.5	6	6,000	43	0.78	potential
MCPA, DIMETHYLAMINE SALT	moderate	moderate	very high	low	low	400	866,000	20	25	5.94	unlikely
METAM-SODIUM	moderate	moderate	very high	very low	very low	510	963,000	6	7	5.98	unlikely
NORFLURAZON	moderate	high	moderate	moderate	high	13	34	353	163	1.53	possible
ORYZALIN	moderate	high	low	moderate	low	15.4	2.5	600	20	0.40	possible
PHOSMET	moderate	high	moderate	moderate	low	2	20	820	19	1.30	possible
PROPICONAZOLE	moderate	moderate	high	moderate	high	510	110	650	115	2.04	possible
SIMAZINE	moderate	high	low	moderate	moderate	36	6.2	130	60	0.79	possible

Table 5C. Low relative risk pesticides

Chem Name	Overall Rank	Rank of toxicity	Rank of solubility	Rank of Koc	Rank of soil half-life	Lowest Toxicity (ug/L)	Water Solubility (mg/l)	Sorption Coefficient (soil Koc)	Soil Half-life (days)	Log (solubility)	Sedment contamination risk
AZOXYSTROBIN	low	low	moderate	moderate	high	56,000	10	581	112	1.00	possilbe
COPPER OXYCHLORIDE SULFATE	low	low	N/A	N/A	N/A	3,750	N/A	N/A	N/A	N/A	potential
EPTC	low	low	high	moderate	very low	1,400	344	200	6	2.54	possible
GLYPHOSATE, ISOPROPYLAMINE SALT	low	low	very high	very high	moderate	1,300	900,000	24,000	47	5.95	potential
IPRODIONE	low	low	moderate	moderate	low	2,300	13.9	700	14	1.14	possible
METHYL BROMIDE	low	low	very high	low	moderate	26,000	13,400	22	55	4.13	unlikely
TRICLOPYR, TRIETHYLAMINE SALT	low	low	very high	low	moderate	14,900	2,100,000	20	46	6.32	unlikely
TRIFORINE	low	low	low	low	low	21,000	6	527	21	0.78	unlikely

__Appendices__

Appendix A. High Relative Risk Pesticides

Azinphos methyl
Use: Insecticide.

Physical properties: Azinphos methyl has a moderate water solubility (29 mg/L), high Koc (1,000), and low half-life in soil (10 days).

Toxicity: The 96-hour LC_{50} ranges from 0.1 to 4,270 μg/L. The lowest value was tested on scud (*Gammarus fasciatus*). For mysid (*Mysidopsis bahia*), the lowest 96-hour LC_{50} was 0.21 μg/L.

Water quality criteria: it is on 303(d) list. The instantaneous maximum water criterion is 0.01 μg/L (USEPA, 1976).

Usage: The average annual use was 48,465 lbs from 1992 to 2001. The amount of use decreased from 1992 to 2001, with the highest amount used in 1992 and the lowest amount used in 2001 (Figure. Azinphos.1). Due to the high amount of use reduction, Azinphos methyl was not on the list of the top 30 pesticides with the highest uses by weight or area from 1998 to 2001. The highest reduction was 81% from 1992 to 2001. Azinphos methyl was used from April to September, with the highest use in July (Figure. Azinphos.2).

Azinphos methyl is applied on almond (52%), walnut (27%), pear (10%), prune (4%), and apple (3%) orchards.

The annual average area of application was 34,382 acres.

Water quality data: Over 600 concentration data were recorded in the SWDB database for azinphos methyl. The highest concentration was 0.054 μg/L in March 1997 (Figures Azinphos.3 and 4). The highest observed concentration was lower than the lowest 96 hour LC_{50} but higher than the USEPA criterion.

Conclusion: Azinphos methyl is ranked as high risk for the surface water quality because of its high toxicity and observed concentrations in the surface water. The rank of risk may be reduced because the annual uses are decreasing, and the heaviest applications were not during winter storm season. However, the risk from the runoff during irrigation season may be high. The risk to sediment contamination is potential because of its high Koc but the short half-life in soils may lower the risk.

Figure Azinphos.1

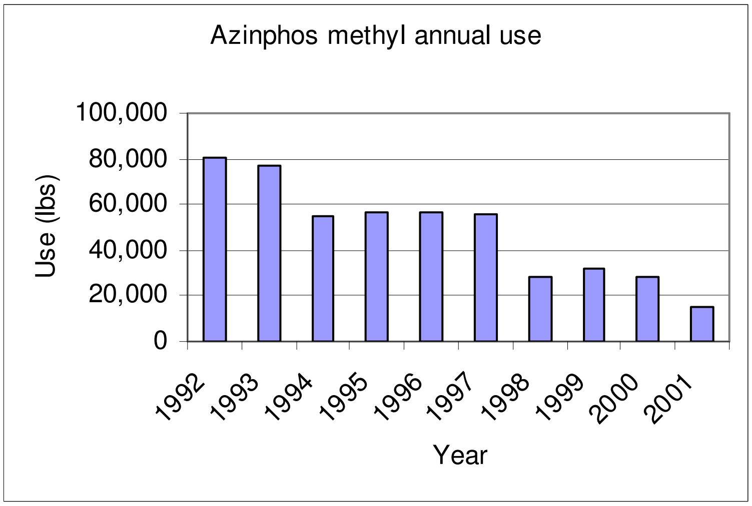


Figure Azinphos.2

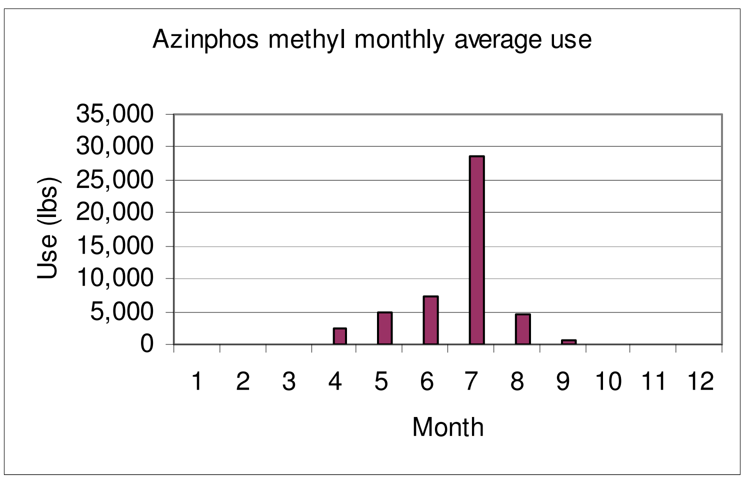


Figure Azinphos.3 (zero indicates the concentration below detection limit)

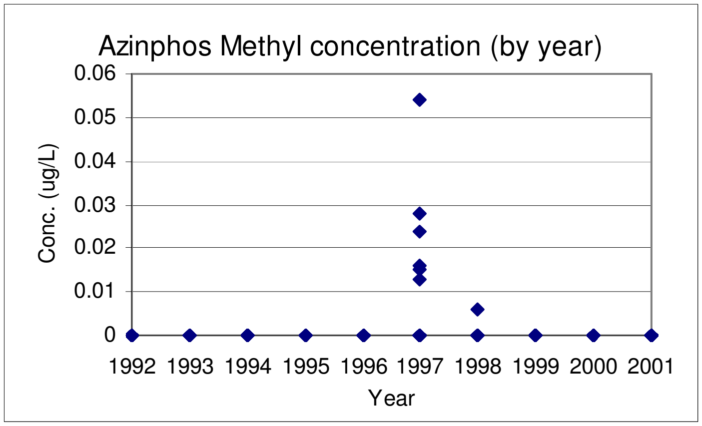
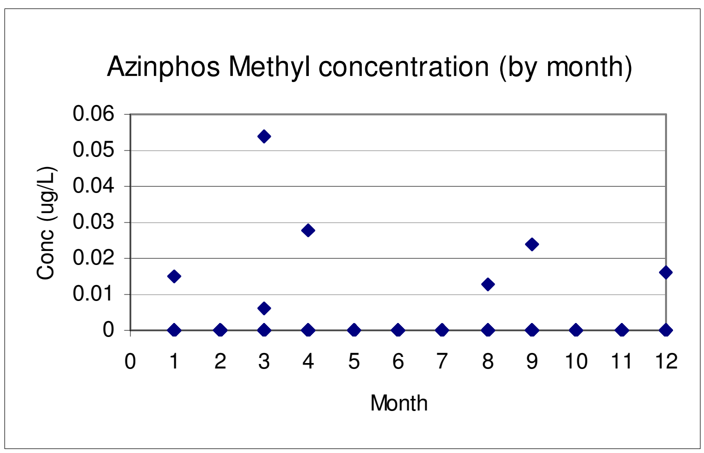


Figure Azinphos.4



Captan
Uses: Fungicide.

Physical properties: Captan has low water solubility (5.1 mg/L), moderate Koc (200), and very low half-life in soil (2.5 days).

Toxicity: The 96-hour LC_{50} ranged from 26 to 8,400 µg/L for fishes and crustaceans (USEPA, 2003). The most sensitive species was brown trout (*Salmo trutta*).

Water quality criteria: The CDFG has not determined a WQC because of insufficient data. The lowest GMAV value was 46 µg/L (CDFG, 1999).

Usage: The average annual use was 153,954 lbs with the highest use (418,083 lbs) in 1998 and the lowest use (68,158 lbs) in 2001 (Figure Captan.1). From 1998, the amount of use gradually decreased. In 2001, the amount of captan reportedly used was about 16% of the amount used in 1998. The use of captan has a strong seasonal pattern, with the highest use occurring in March (Figure Captan.2). Very low amounts of captan were reportedly used between August and January.

The annual average area to which captan was applied was 53,850 acres. In 2001, the applied acreage was 26,483 acres, 23% of the total area used in 1998.

The major uses of captan are on almond (54%) and prune (44%). The highest use was in March on prune during full-bloom season. February and April also have relatively high amounts of reported use.

Water quality data: There are no captan concentration data in the SWDB database.

Conclusion: Captan is ranked as high risk to surface water quality because of its high toxicity and high applications during the winter storm season. The decrease in amount of captan reportedly used and its low water solubility could reduce the risk level. Sediment contamination is possible because of moderate Koc, but the short half-life in soil may reduce the risk of sediment contamination.

Uncertainty: The risk assessment has high uncertainty because there is no water column concentration data.

Figure Captan.1

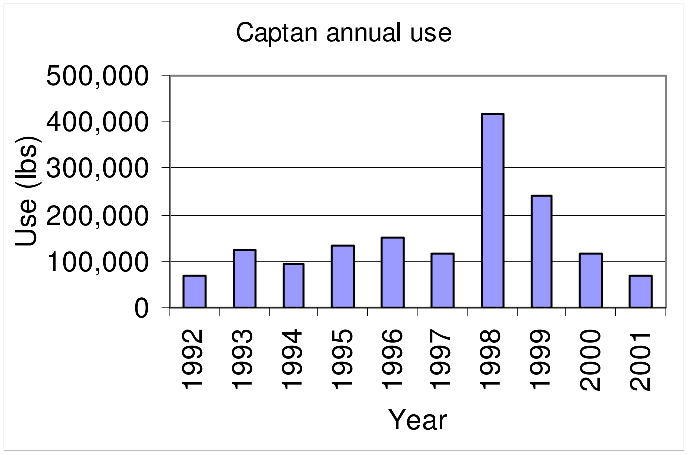
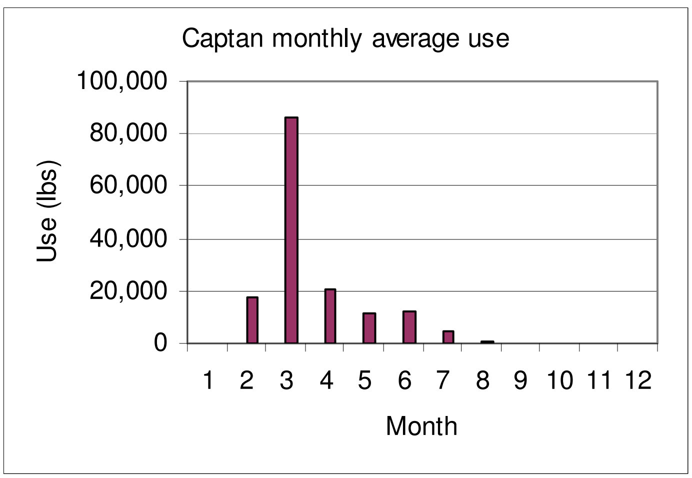


Figure Captan.2



Carbofuran
Uses: Insecticide, acaricide, and nematicide. 80% of the total usage was in granular formulations. Granular formulations were phased out in September 1991 because of high avian toxicity.

Physical properties: Carbofuran has high water solubility (351 mg/L), low Koc (22), and moderate soil half-life (50 days).

Toxicity: The 96-hour LC_{50} ranges from 7.3 to 1,990 µg/L and the most sensitive species is pink shrimp (*Penaeus duorarum*) (EPA, 2003).

Water quality criteria: The CDFG proposed an interim WQC of 0.5 µg/L and had insufficient data for determining the CCC and CMC (CDFG, 1992). The DPR reported on the environmental fate of carbofuran in 2002.

Usage: From 1992 to 2001, the average annually application was 46,217 lbs. The highest amount used was 68,471 lbs in 1993 and the lowest use was 2,650 lbs in 2001 (Figure Carbofuran.1). The amount of use in 2001 was only about 4% of the usage in 1993. The amount of application has reduced significantly from 1998. Therefore, carbofuran was not on the list of the 30 highest used pesticides. The applications changed with month with about 65% of the annual use in May (Figure Carbofuran.2). There were no applications in February, November, and December.

The average annual area of application was 93,591 acres with the highest acreage (136,849 acres) in 1993.

The major applications are on rice, alfalfa, cotton, and grapes. Approximately 95% of total annual carbofuran was applied on rice and only 2% of the annual use was on alfalfa and other crops. However, the applications on rice were reduced to 23% in 2000 from 1993. In 2001, no carbofuran used on rice was reported in the DPR PUR database.

Water quality data: Over 1,500 carbofuran concentration data were recorded in the DPR SWDB database from 1992 to 2003 (Figures Carbofuran.3 and Carbofuran.4). The highest concentration (3.6 µg/L) was observed in May 1999. The highest observed concentration was higher than the CDFG proposed interim WQC.

Conclusion: Carbofuran is ranked as high risk to surface water quality because of its high toxicity and high observed concentrations. However, the risk may be reduced to moderate because of the reported decreased amount of carbofuran use and because no carbofuran applied during the winter storm season. Carbofuran has a low potential to contaminate sediment because of its low Koc and moderate half-life in soil.

Figure Carbofuran.1

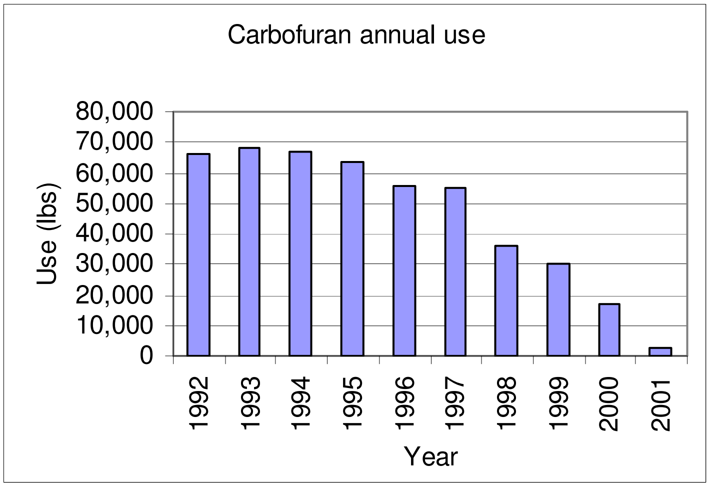


Figure Carbofuran.2

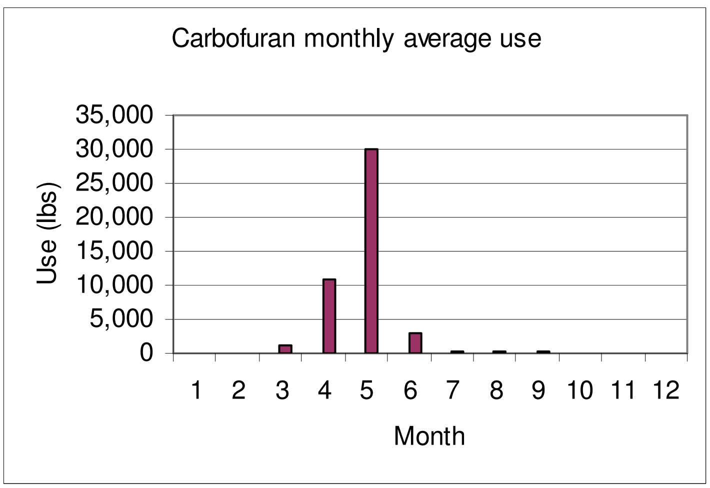


Figure Carbofuran.3 (zero indicates the concentration below detection limit)

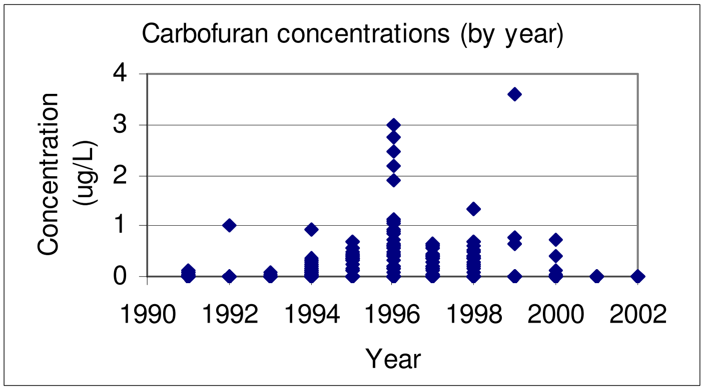
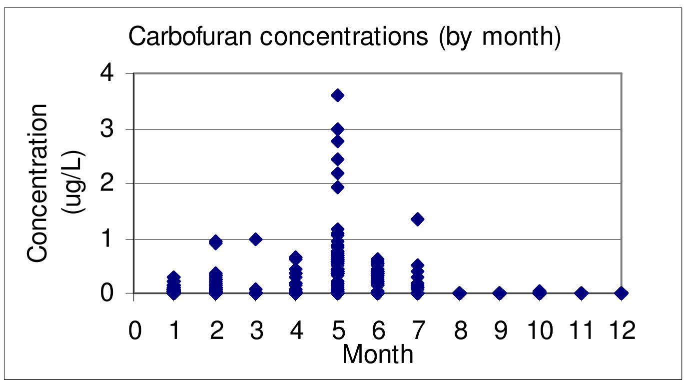


Figure Carbofuran.4



Chlorothalonil
Uses: Fungicide.

Physical properties: Chlorothalonil has very low water solubility (0.6 mg/L), high Koc (1,380), and low half-life in soil (30 days).

Toxicity: The 96-hour LC_{50} for chlorothalonil ranged from 26 to 195 μg/L for fishes and crustacean (USEPA, 2003). The lowest value (26 μg/L) was tested on Eastern oyster (*Crassostrea virginica*).

Water quality criteria: The CDFG report has no WQC calculated for chlorothalonil due to insufficient data (CDFG, 1999). The most sensitive species test GMAV (genus mean acute value) was 21 μg/L for galaxiid fish (*Galaxia spp.*).

Usage: The average annual use was 75,565 lbs with the highest use (133,285 lbs) in 1992 and lowest use (18,012 lbs) in 2001 (Figure Chlorothalonil.1). The amount used in 2001 was only 14% of the amount used in 1992. The monthly use showed that the high use was in March, July, and August (Figure Chlorothalonil.2). The major use in March was on prunes and the major use in July and August was on tomatoes.

The major crops to which chlorothalonil was applied include tomato (68%) and prune (25%).

The average annual acreage to which chlorothalonil was applied was 39,850 acres.

Water quality data: There were 75 concentration data points collected from 1996 to 1998. None of the samples exceeded the LOQ (0.035 and 0.48 μg/L).

Conclusion: Chlorothalonil is ranked as high risk because of its high toxicity. The annual amount of use has decreased in recent years and none concentration data exceeded the lowest toxicity value, so the risk may be reduced. The runoff from prune orchards in March may be high because of high applications during storm season. The observed concentrations did not exceed the LOQ, one of the reasons might be its low water solubility. The risk is potential for sediment contamination because of its high Koc.

Figure Chlorothalonil.1

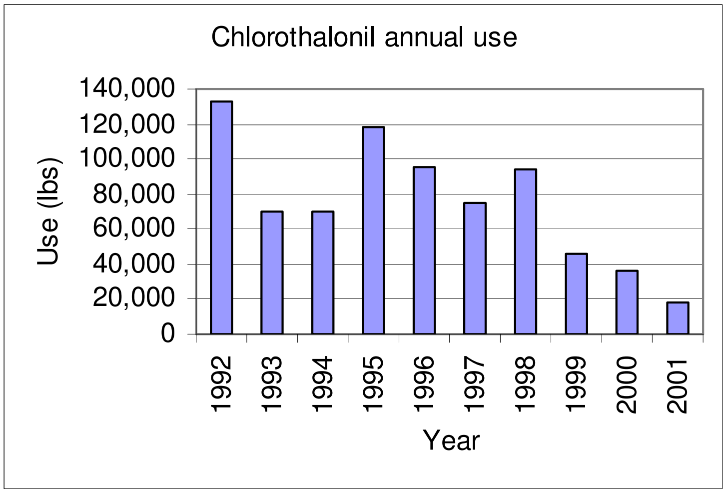
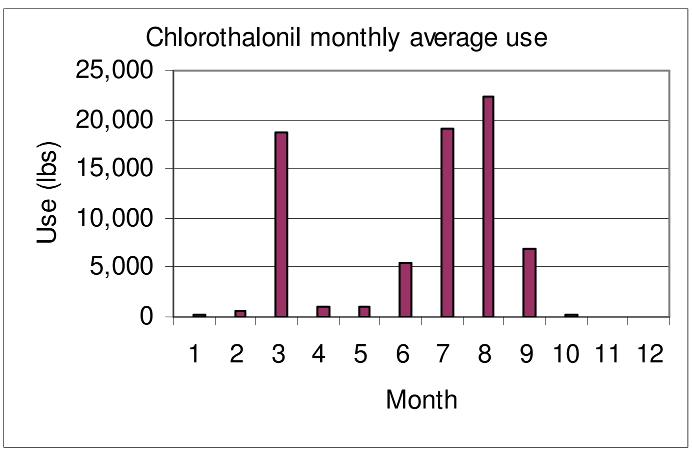


Figure Chlorothalonil.2



Diuron
Use: Herbicide. Diuron was not selected in the initial target list because of its low amount use based on total weight and area. DPR staff suggested that diuron be included in the target list because it has been detected in surface waters.

Physical properties: Diuron has a moderate water solubility (42 mg/L), moderate Koc (477), and long half-life in soil (90 days).

Toxicity: The 96-hour LC_{50} ranges from 160 to 300,000 µg/L for fishes and crustaceans. The lowest LC_{50} value was tested on scud (*Gammarus fasciatus*). For mysid (*Mysidopsis bahia*), the lowest 96-hour LC_{50} was 560 µg/L. The EC50 ranges from 2.4 to 95 µg/L tested on aquatic plants between 72 hours and 14 days. The lowest 96-hour EC50 value was 2.4 µg/L tested on green algae (*Selenastrum capricornutum*).

Water quality criteria: no water quality criteria for aquatic organisms proposed.

Usage: The average annual use was 21,438 lbs from 1992 to 2001. The amount of use decreased slightly from 1992 to 2001 with the highest amount of use in 1993 (24,851 lbs) and the lowest use in 2001(17,307 lbs). The amount of use decreased about 23% from 1999 to 2001 (Figure Diuron.1). Relatively high uses were reported to occur from November to April (Figure Diuron.2).
Diuron is mainly applied on walnut (46%), alfalfa (36%), and olive (11%).

The annual average area application was 23,962 acres.

Water quality data: There were 528 records of diuron concentration in the SWDB database and 44% of the data exceeded the LOQ (0.01 to 1 µg/L). The highest concentration in surface water was 30.6 µg/L observed in February 1992 (Figures Diuron.3 and 4). The maximum concentration was much lower than the lowest 96-hr LC_{50} (160 µg/L) but much higher than the lowest EC50 value (2.4 µg/L).

Conclusion: Diuron is ranked as high risk because of its high toxicity to aquatic plants. Although the annual use of diuron is not in the top 30 pesticides, the amounts of use were relatively high in both total weight and total area. The heavy usage of diuron during winter storm season (December to February) poses the potential for runoff risk. The observed concentration data from surface water confirmed the risk because over 40% of the observed data exceeded the LOQ. Diuron is often used in combination with other pesticides, such as bromacil and hexazinone, but the toxicity of the combined uses is not addressed in this evaluation because no sufficient information available. Since diuron is an herbicide, the contamination risk to aquatic plants is high. Diuron is possible to contaminate sediment because of its moderate Koc and moderate half-life in soils. Diuron has been detected in groundwater in low concentrations (2 to 3 µg/L).

Figure Diuron.1

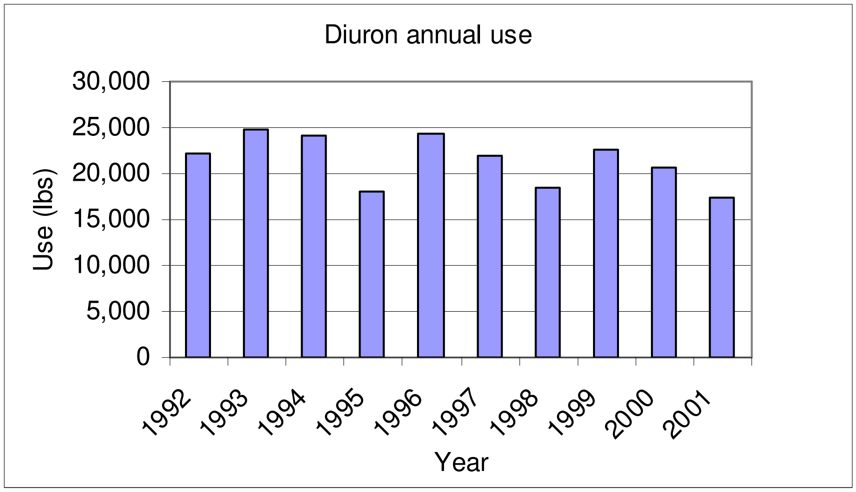


Figure Diuron.2

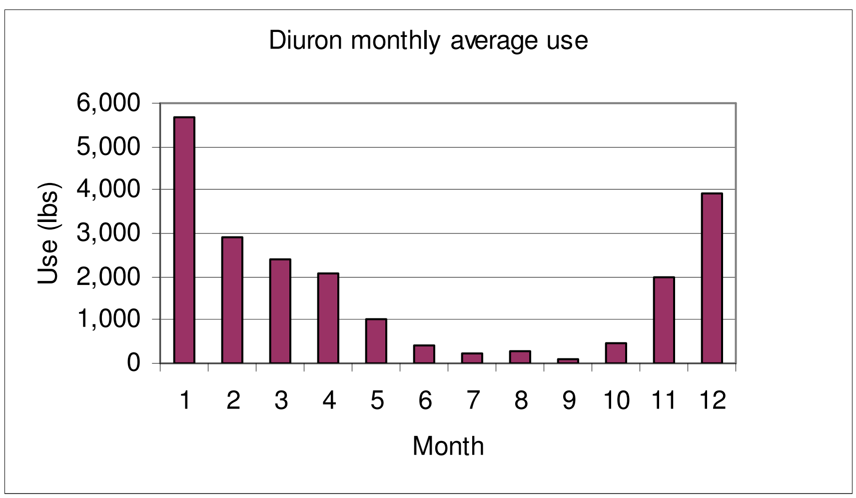


Figure Diuron.3 (zero indicates the concentration below detection limit)

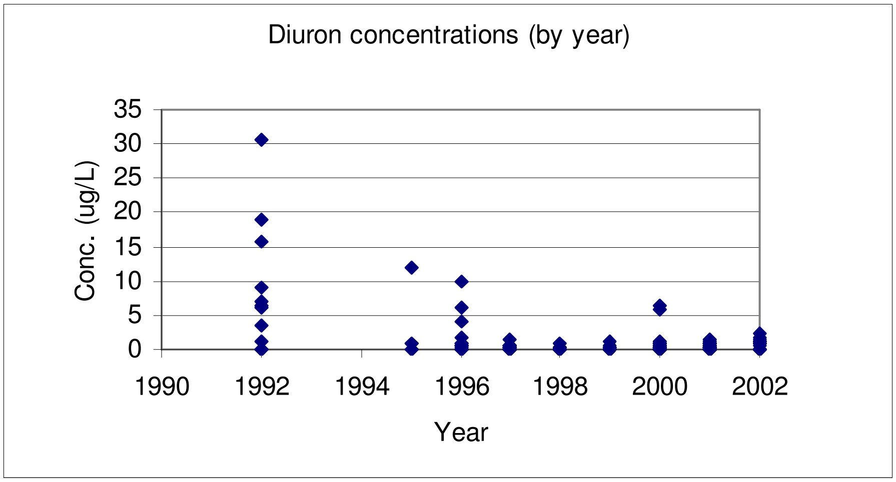
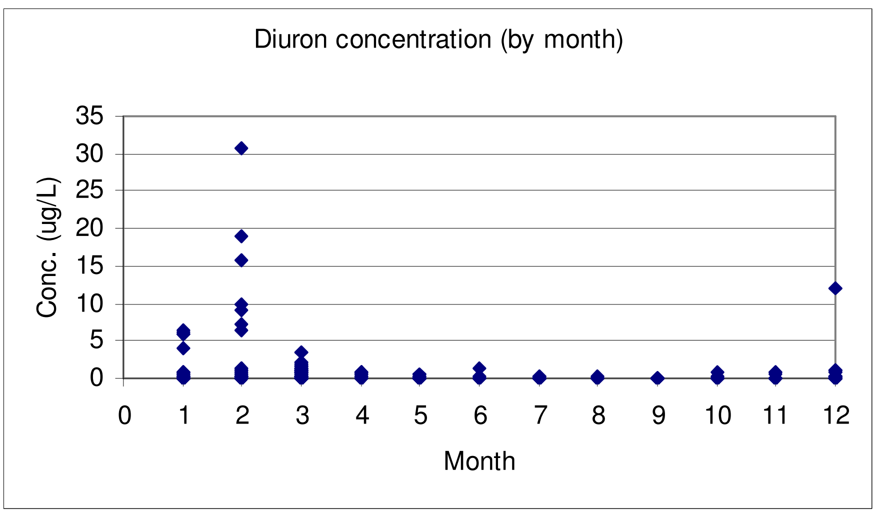


Figure Diuron.4



Esfenvalerate
Uses: Insecticide, one of pyrethroids.

Physical properties: Water solubility is 0.0002 mg/L, Koc is 5,273, and soil half-life is 35 days (ARS database, 2002). Esfenvalerate is insoluble in water, highly adsorbed to soil particles, and persists moderately long in soils. The half-life ranges from 15 days to three months, depending on soil type. The half-life of esfenvalerate in water was reported to range from 4 to 15 days (EXTOXNET, 2003).

Toxicity: The 96-hour LC50 for esfenvalerate ranges from 0.07 to 0.23 µg/L (USEPA, 2003). The lowest toxicity value tested rainbow trout (*Oncorhynchus mykiss*). Bioaccumulation produced concentrations of esfenvalerate in rainbow trout were about 400 times higher than the background concentration (EXTOXNET, 2003).

Water quality criteria: The CDFG did not propose water quality criteria because of insufficient data. The CDFG reported that the GMAV (genus mean acute value) was 0.26 µg/L for rainbow trout (*Oncorhynchus mykiss*).

Usage: The average annual esfenvalerate use was 4,880 lbs with the highest use in 1997 and lowest use in 1992 (Figure Esfenvalerate.1). The reported annual amount of esfenvalerate increased about 1.7 times from 2,424 lbs in 1992 to 6,586 lbs in 1997. From 1997 to 2001, the amount of use decreased about 21% from 6,586 lbs to 5,202 lbs. However, from 1997 to 2001, the lowest use was in 2000 and the annual amount of use varied. The reported monthly use of esfenvalerate showed that the highest use was in July and lowest use was in November (Figure Esfenvalerate.2). Relatively high use months include January, June, and August.

The average annual application area is 97,064 acres from 1992 to 2001.

The major reported crops of use include prune (17%), walnut (16%), tomatoes (16%), almond (13%), beans (9%), peach (8%), and pear (5%). The highest uses in January include prune, almond, peach, and pear. The highest uses in July include walnut, tomatoes, and sunflowers.

Water quality data: The SWDB had 64 samples with associated esfenvalerate concentration data from 1996 to 1998. None of the samples was over the LOQ (0.019 µg/L). Monitoring results for the Sacramento and San Joaquin Delta from June 2002 to May 2003, also showed no esfenvalerate detected over the LOD (0.007 µg/L).

Conclusion:
Esfenvalerate is ranked as high risk to the surface water because of its very high toxicity to aquatic organisms, no clear decreasing trend of use in recent years, and relatively high use in January. Although its low water solubility results in almost no detectable levels in surface water samples, there is a high potential risk for sediment contamination because of esfenvalerate's high Koc and moderate half-life.

Figure Esfenvalerate.1

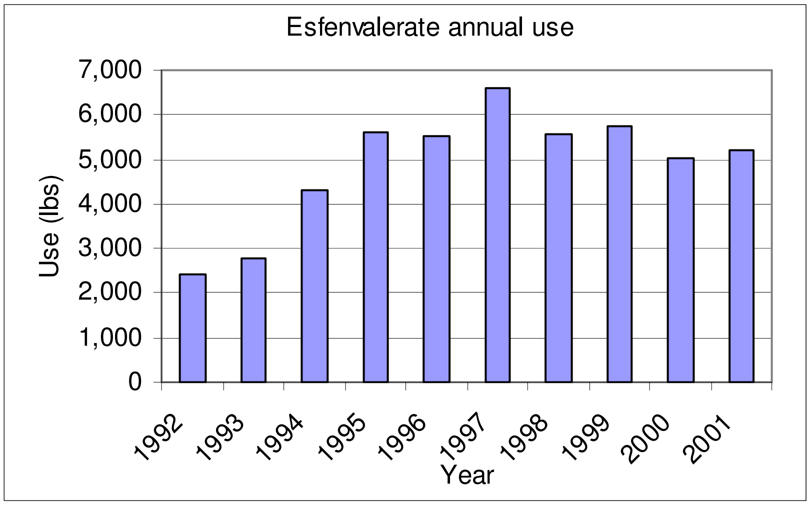
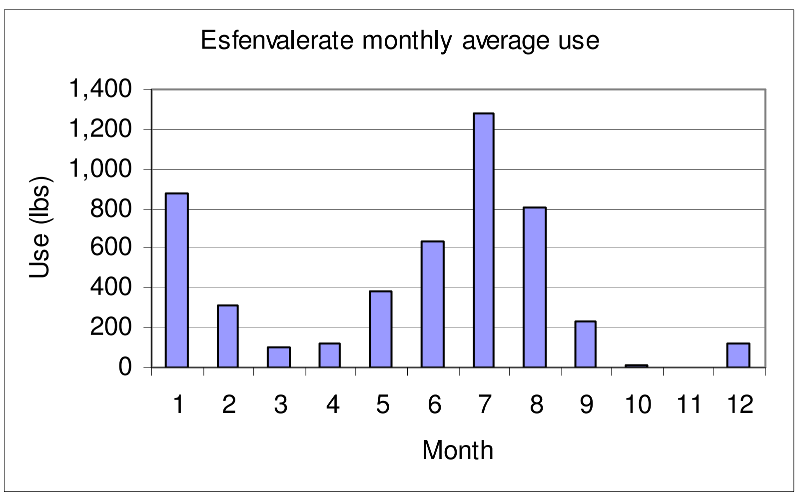


Figure Esfenvalerate.2



Lambda cyhalothrin
Uses: Insecticide, one of the pyrethroids.

Physical properties: Lambda cyhalothrin has very low water solubility (0.005 mg/L), very high Koc (180,000), and low half-life in soil (30 days).

Toxicity: The 96-hour LC_{50} values ranged from 0.0041 to 11.2 µg/L (USEPA, 2003). The most sensitive species was mysid (*Mysidopsis bahia*).

Usage: The use of lambda cyhalothrin started in 1998. From 1998 to 2001, the average annual use was 5,710 lbs and the highest use was 10,595 lbs in 2000 (Figure Lambda.1). The major application reportedly occurred between March and September with the highest use in May (Figure Lambda.2). The major applications of lambda cyhalothrin are on rice (62%) and tomatoes (20%).

The average annual use was 158,405 acres from 1998 to 2001.

Water quality data: The SWDB has 18 samples collected in 2000 with lambda cyhalothrin concentration data and none of the data exceeded the LOQ (0.01 µg/L).

Conclusion: Lambda cyhalothrin is ranked as high risk because of its very high toxicity. Because of its very low water solubility and very high Koc value, the concentrations in water are difficult to be detected. Sediment contamination could be potential because of its very high Koc value.

Figure Lambda.1

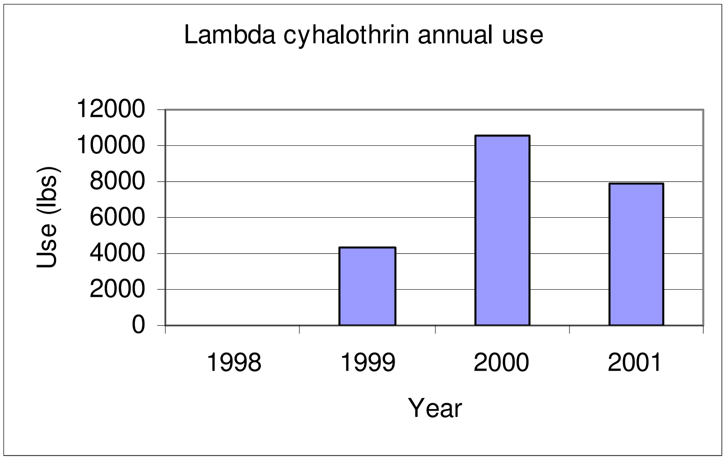
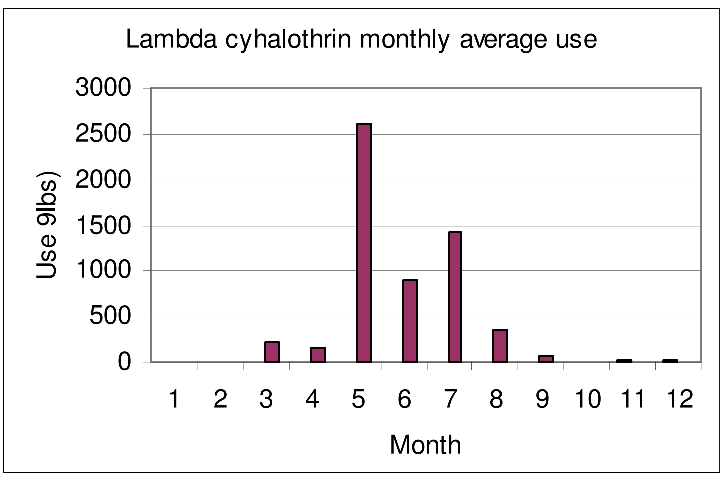


Figure Lambda.2



Malathion

Uses: Insecticide.

Physical properties: Malathion has high water solubility (130 mg/L), high Koc (1,800), and low soil half-life (one day).

Toxicity: The 96-hour LC_{50} ranged from 0.5 to 11,700 µg/L (USEPA, 2003). The most sensitive species was scud (*Gammarus fasciatus*).

Water quality criteria: The CDFG proposed a CMC (0.43 µg/L) but no CCC, because of insufficient data (CDFG, 1998).

Usage: The average annual use was 33,063 lbs between 1992 and 2001. The highest use was 64,744 lbs in 1992 and the lowest use was 11,603 lbs in 2000 (Figure Malathion.1). The amount of use in 2000 was about 17% of the amount used in 1992. In 2001, the amount of use (24,721 lbs) was higher than the amount used in 2000. Because the high reduction of use, malathion was not on the list of 30 highest used pesticides between 1998 and 2001. The monthly application data shows high uses between March and September and lower uses from October to February (Figure Malathion.2). The highest use was in August and second highest use was in March.

The average application area was 17,817 acres. The highest application area was 31,802 acres in 1992.

The major applications of malathion were on walnut (35%), alfalfa (34%), rice (16%), and beans (3%). However, the applications on alfalfa, rice, and beans are highly reduced since 1998.

Water quality data: The SWDB has over one thousand malathion concentration data. The data were collected from 1991 to 2002 and the highest concentration (6 µg/L) was observed in May 1996 (Figures Malathion.3 and Malathion.4). Approximately 1% of data exceed the CMC (0.43 µg/L).

Conclusion: Malathion is ranked as high risk to surface water quality because it has very high rank of toxicity and high concentrations have been observed in the surface water. The heaviest application occurs during the irrigation season, therefore the risk due to irrigation runoff may be high. However, the risk may be lower because of lower use in recent years. Malathion has a potential risk to contaminate sediments because of its high Koc, but the short half-life in soil may lower the risk, depending on the soil conditions.

Figure Malathion.1

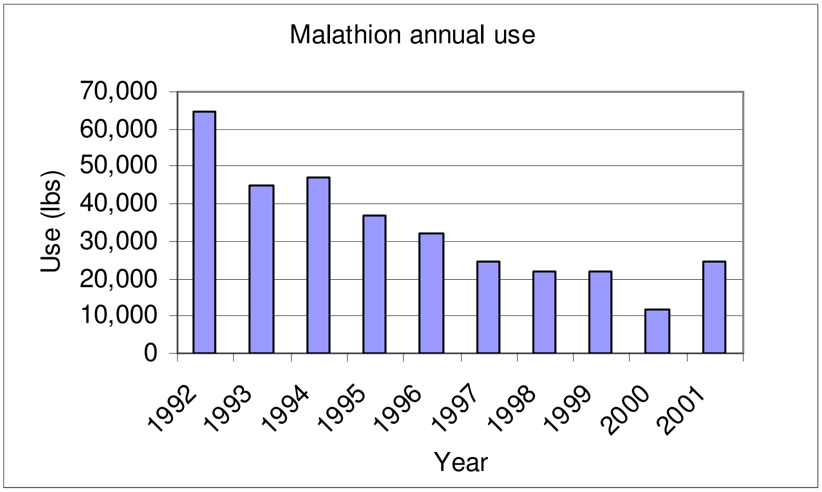


Figure Malathion.2

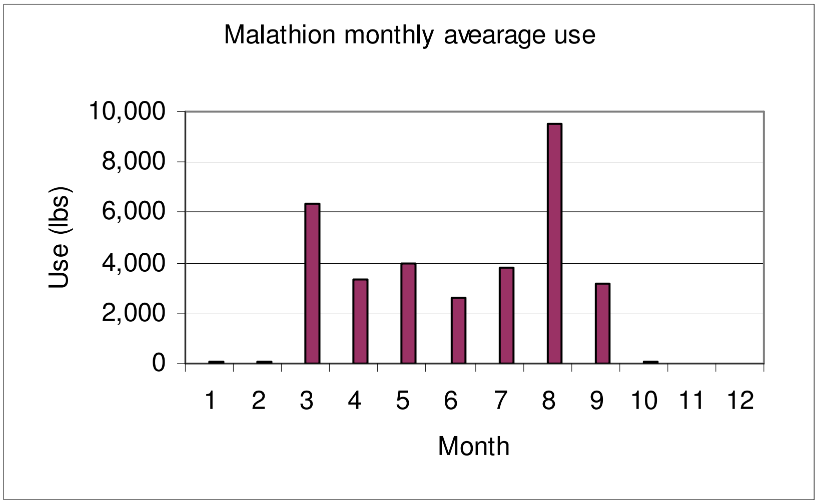


Figure Malathion.3 (zero indicates the concentration below detection limit)

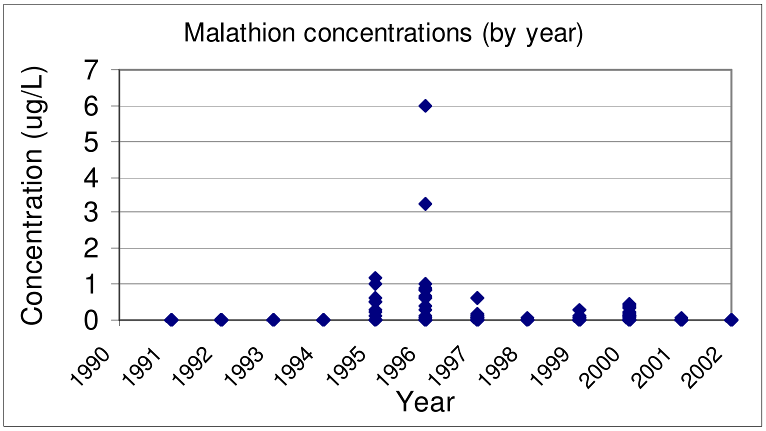
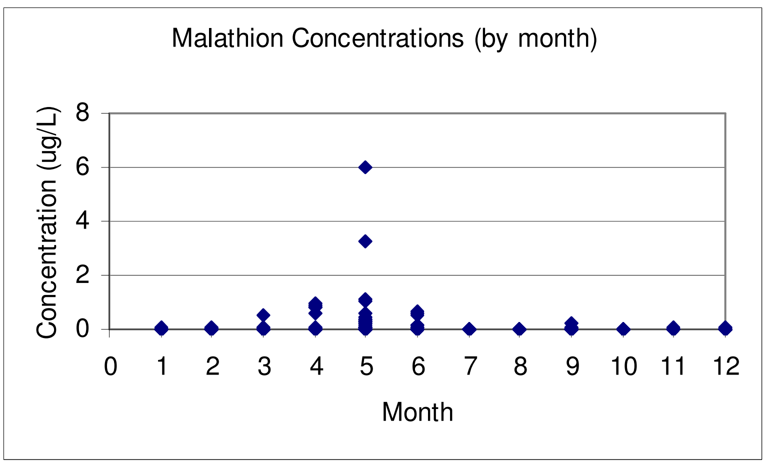


Figure Malathion.4



Maneb
Uses: Fungicide.

Physical properties: Maneb has low water solubility (6 mg/L), moderate Koc (240), and moderate half-life (30 days) in soil.

Toxicity: The 96-hour LC_{50} ranged from 33 to 1,000 µg/L (USEPA, 2003). The most sensitive species was mysid (*Mysidopsis bahia)*.

Water quality criteria: The CDFG report reviewed the data but did not calculate the WQC because of insufficient data (CDFG, 2003). The lowest GMAV was 330 µg/L for rainbow trout.

Usage: The annual uses of maneb from 1992 to 2001 are shown in Figure Maneb.1. The average annual use was 222,917 lbs between 1992 and 2001. The amount of use increased from 1992 to 1998 and then decreased in 1999 and 2001. The reductions of maneb use were mainly on walnut and almond in 1999 and 2001. The highest annual use was 434,841 lbs in 2000 and the lowest annual amount used was 16,774 lbs in 1992. Heavy applications were reported between February and May with the highest use in April (Figure Maneb.2).

The average annual application area was 104,923 acres with the highest use (232,651 acres) in 1998.

The major crops on which maneb was reportedly applied were on walnut (73%) and almond (25%).

Water quality data: There were no concentration data for maneb in the DPR SWDB.

Conclusion: Maneb is ranked as high risk to surface water quality because of high toxicity, high amount of use, and relatively high use on orchards during the winter storm season. The overall risk of maneb to contaminate surface water may be lower than the risk to sediment contamination because of low water solubility, moderate Koc and half-life in soils.

Figure Maneb.1

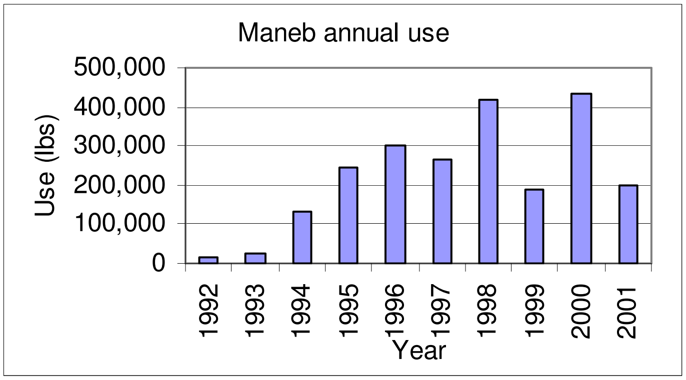
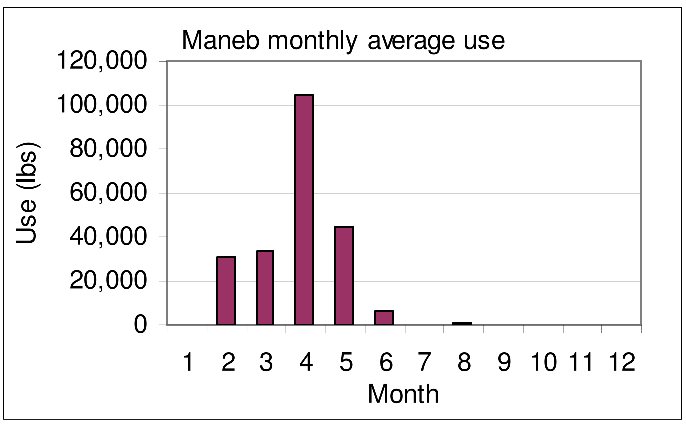


Figure Maneb.2



Methidathion
Uses: Insecticide.

Physical properties: Methidathion has a very high water solubility (220 mg/L), moderate Koc (400), and low half-life in soil (7 days).

Toxicity: The 96-hour LC_{50} ranges from 0.7 to 7,500 µg/L and the most sensitive freshwater species was a mysid (*Mysidopsis bahia*).

Water quality criteria: The CDFG did not develop CCC and CMC values because of insufficient data.

Usage: The average annual use of methidathion was 47,594 lbs. The highest reported amount used was 98,096 lbs in 1993 and the lowest amount used was 7,260 lbs in 2001 (Figure Methidathion.1). The amount used in 2001 is only 7% of the amount used in 1993. Methidathion was not on the list of the highest 30 pesticides used between 1998 and 2001. The application data shows a strong seasonal pattern with the highest use in January and February (Figure Methidathion.2).

The average annual area to which methidathion was applied is 38,181 acres with the highest use of 62,866 acres in 1992.

The major applications were on prune (34%), almond (30%), peach (15%), walnut (13%), and pear (3%) orchards.

Water quality data: Over 1,200 concentration data are recorded in the DPR SWDB database. The highest concentration was 15.1 µg/L observed in February 1992 (Figures Methidathion.3 and Methidathion.4). Most of the detected concentrations occurred in January and February.

Conclusion: Methidathion is ranked as high risk to surface water quality because of its high toxicity, application time (during the storm season), and high-observed concentrations in surface waters. Although the amounts of use decreased over time, the maximum observed concentrations (1.58 µg/L) was higher than the lowest toxicity value (0.7 µg/L). Sediment contamination is possible because of its moderate Koc and low half-life in soil.

Figure Methidathion.1

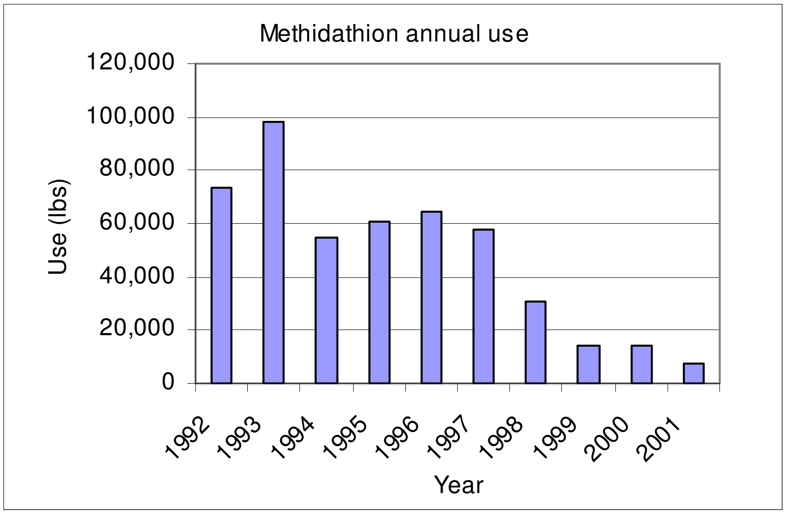


Figure Methidathion.2

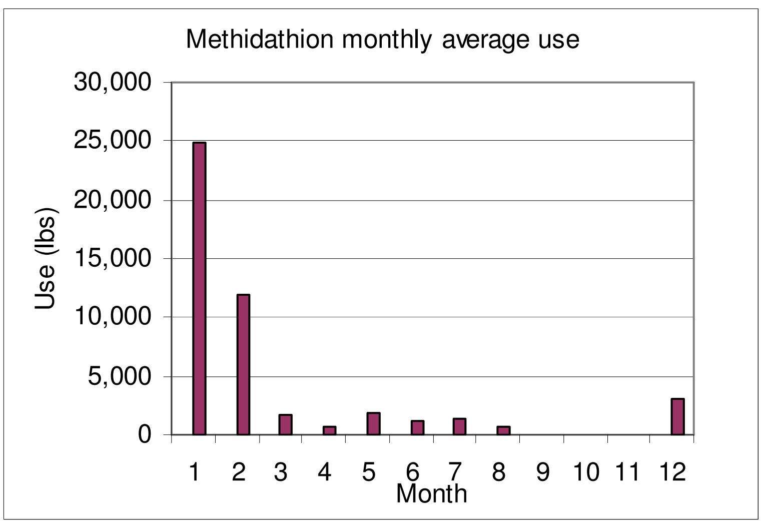


Figure Methidathion.3 (zero indicates the concentration below detection limit)

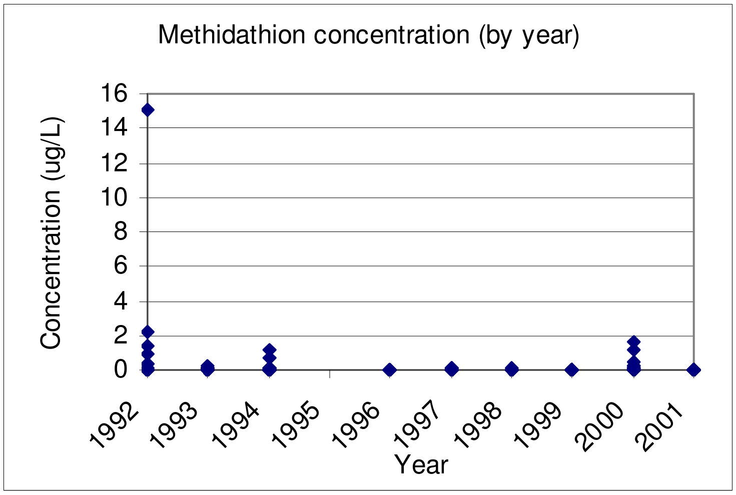
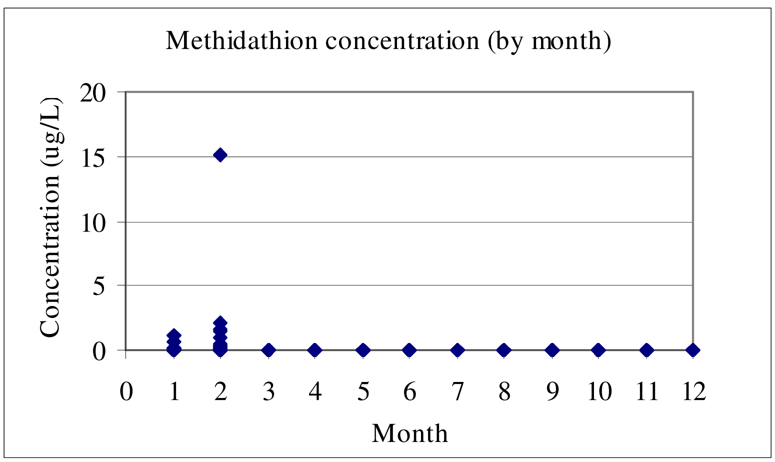


Figure Methidathion.4



Methyl parathion
Uses: Insecticide.

Physical properties: Methyl parathion has moderate solubility (60 mg/L), high Koc (5,100), and very low half-life (5 days) in soil.

Toxicity: The 96-hour LC_{50} ranged from 0.78 to 12,000 µg/L. The most sensitive species was mysid (*Mysidopsis bahia).*

Water quality criteria: The CDFG proposed 0.08 µg/L as an interim water quality criterion for methyl parathion. The report indicated that the acceptable level could be lower because of cumulative toxicity.

Usage: The annual average use was 31,057 lbs from 1992 to 2001, with the highest use in 1993 and the lowest use in 2000 (Figure Parathion.1). The amount used in 2000 was only 17% of used in 1993. Overall, the use has decreased from 1993. Methyl parathion was not on the list of highest 30 pesticides used between 1998 and 2001. There were almost no uses in February, March, and November (Figure Parathion.2). High uses were between May and July, with the highest use in May.

The annual average area to which methyl parathion was applied was 32,581 acres.

The major crops include peach (25%), walnut (23%), and prune (19%) orchards.

Water quality data: Over 1,000 samples with methyl parathion concentration data exist in the SWDB. The maximum concentration was 0.187 µg/L and the highest concentrations were detected in June 1995. The most recent data indicated that the methyl parathion concentrations were much lower than in previous years. Between 2000 and 2002, 530 concentration data were recorded in the SWDB, but none of them were over the detection limit.

Conclusion: Methyl parathion is ranked as high risk because it has very high toxicity and observed concentration exceeded the proposed WQC. The risk may be lower because the amount of annual use was reduced in recent years and no heavy uses were applied in winter storm season. The risk for sediment contamination is likely high because of its high Koc but it has very low half-life in soil that may lower the risk.

Figure Parathion.1

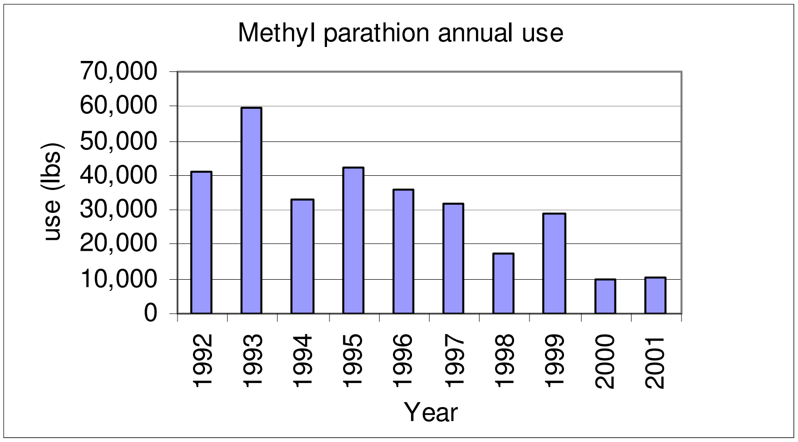


Figure Parathion.2

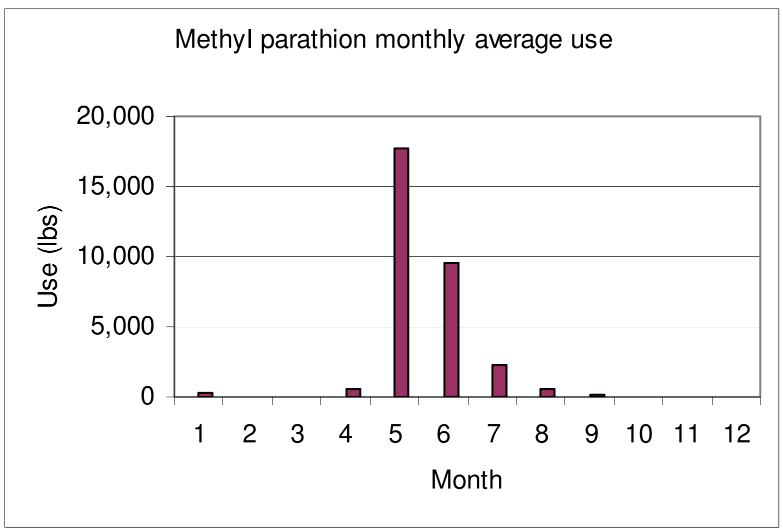


Figure Parathion.3 (zero indicates the concentration below detection limit)

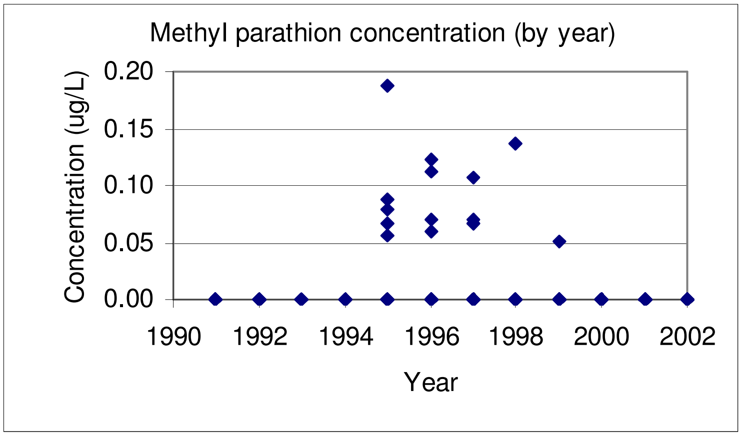
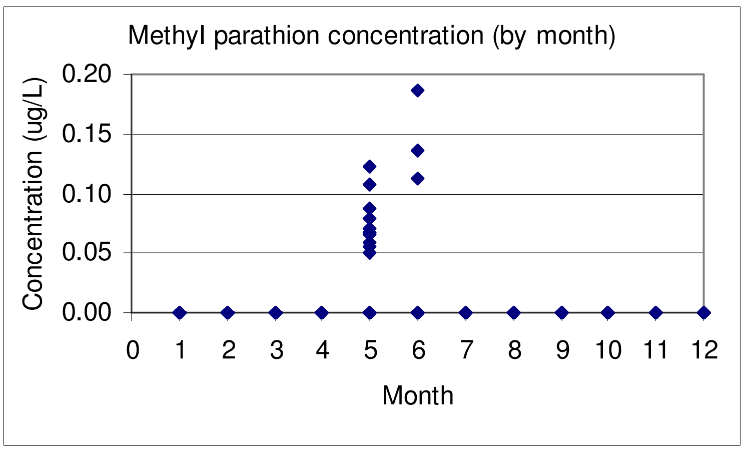


Figure Parathion.4



Molinate
Uses: Herbicide for rice field

Physical properties: Molinate has relatively high solubility (970 mg/L), moderate Koc (190), and low half-life (21 days) in soil.

Toxicity: The 96-hour LC_{50} ranged 760 to 34,000 µg/L. The most sensitive species was mysid (*Mysidopsis bahia*). The EC50 ranges from 220 to 21,100 µg/L tested on aquatic plants between 96 hours to 14 days. The lowest EC50 value was from a 96-hour test on green algae (*Selenastrum capricornutum*).

Water quality criteria: The CDFG recommended a water quality criterion is 13 µg/L (CDFG, 1990). It is the half of the value tested on mysid (*Neomysis mercedis)* for 42-day no observed effect concentration (NOEC). Molinate is applied to rice fields along with thiobencarb, therefore, the criteria were determined considering the effects of both herbicides.

Usage: The amounts of molinate used decreased from 1992 to 2001 with an average annual use of 1,159,866 lbs (Figure Molinate.1). The highest use was 1,473,122 lbs in 1994 and the lowest use was 694,740 lbs in 2001. The reduction was about 47% in weight. Molinate is used just after rice fields are flooded and the application timing is from April to June (Figure Molinate.2). The highest monthly use was in May. There was no reported molinate use from October to January.

The average annual acreage applied was 296,984 acres from 1992 to 2001.

Water quality data: More than one thousand samples with molinate concentration data are reported in the DPR SWDB. Although, in general, concentrations decreased from 1995 to 2002, many of the sample concentrations were still higher than the CDFG recommended value (13 µg/L). The high concentrations were observed in May and June (Figures Molinate.3 and Molinate.4).

Conclusion: Molinate is ranked as high risk because of its high toxicity when combined with the use of thiobencarb. Observed concentration data exceeded the proposed water quality criteria. Molinate was also listed on the 303(d) list. Detailed studies have been done for many years and regulations have been enforced to reduce the amount of molinate into surface water. Molinate is going to be phased out in 2008.

The risk of sediment contamination is possible because of the moderate Koc. Suspended particles had high molinate residues.

Figure Molinate.1

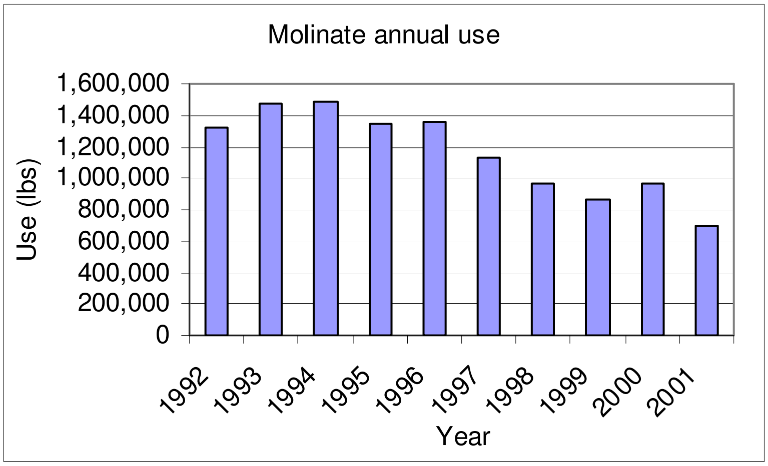


Figure Molinate.2

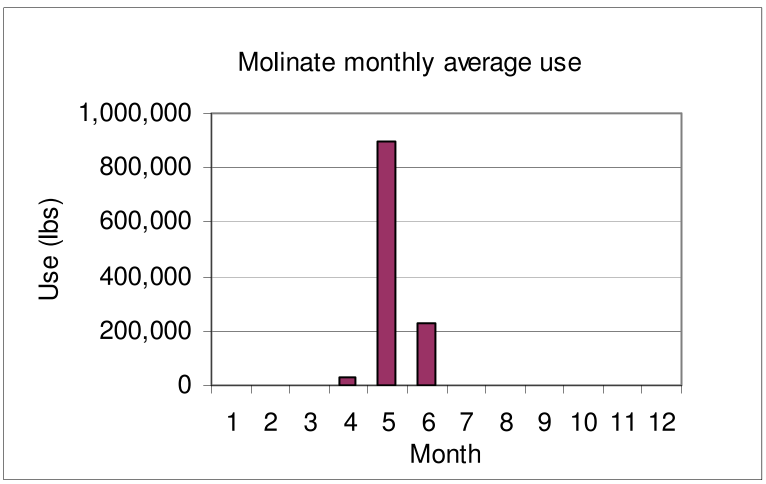


Figure Molinate.3 (zero indicates the concentration below detection limit)

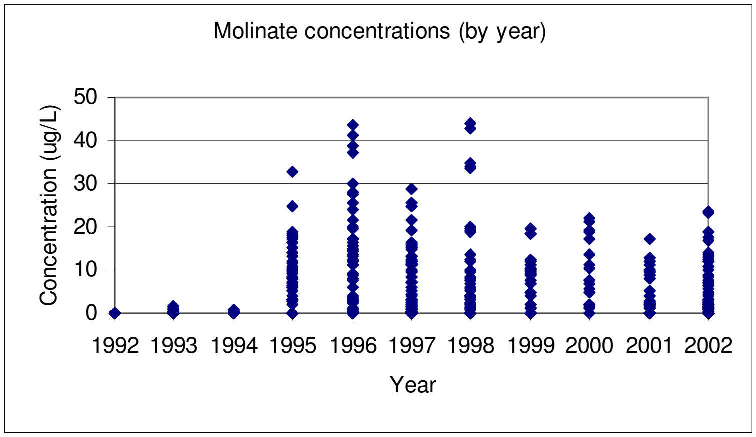
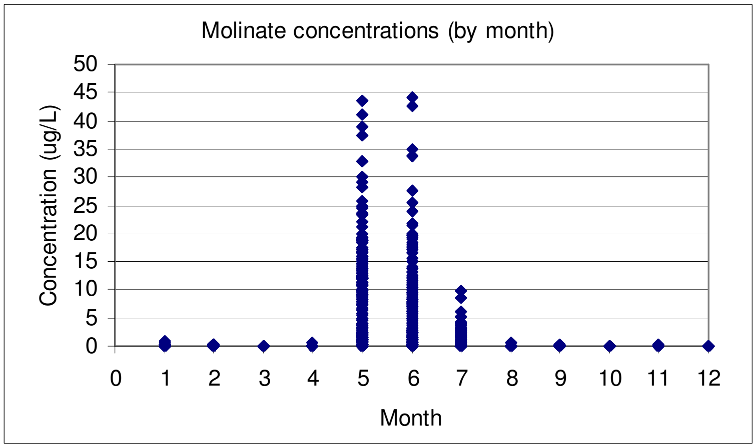


Figure Molinate.4



Oxyfluorfen
Uses: Herbicide.

Physical properties: Oxyfluorfen has very low water solubility (0.1 mg/L), very high Koc (100,000), and moderate half-life in soil (35 days).

Toxicity: The 96-hour LC_{50} ranges from 31.7 to 1000,000 µg/L. The most sensitive species was grass shrimp (*Palaemonetes pugio*). The EC50 ranges from 0.29 to 2.9 µg/L) tested on aquatic plants between 96 hours and 10 days. The lowest EC50 value was from a 96-hour test on green algae (*Selenastrum capricornutum*).

Water quality criteria: Not available.

Usage: The annual average use was 22,814 lbs from 1992 to 2001. The highest use was 30,613 lbs in 1996 and the lowest use was 15,507 lbs in 2001 (Figure Oxyfluorfen.1). The amount used in 2001 was about 51% of the amount used in 1996. The high use months include November, December, January, and February (Figure Oxyfluorfen.2).

The major crops to which oxyfluorfen is applied are almond (47%), prune (17%), walnut (15%), and pistachio (3%) orchards.

The annual average application area was 106,836 acres.

Water quality data: There were no concentration data for oxyfluorfen in the SWDB.

Conclusion: Oxyfluorfen is ranked as high risk because of its high toxicity, high potential to occur in field runoff during the winter storm season, and no high reduction of annual use in recent years. Since it has very low water solubility and its half-life in water is short, the concentration of oxyfluorfen in water may be low. The risk to sediment contamination is potential because of its high Koc and moderate soil half-life. Future monitoring will be useful in risk determination.

Figure Oxyfluorfen.1

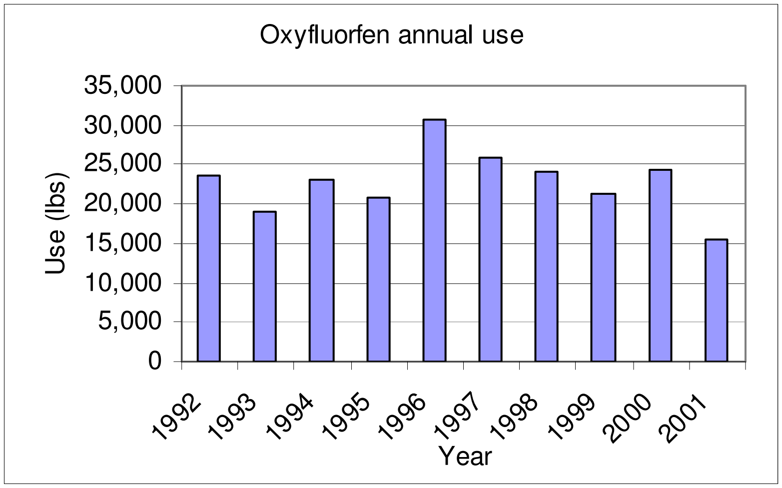
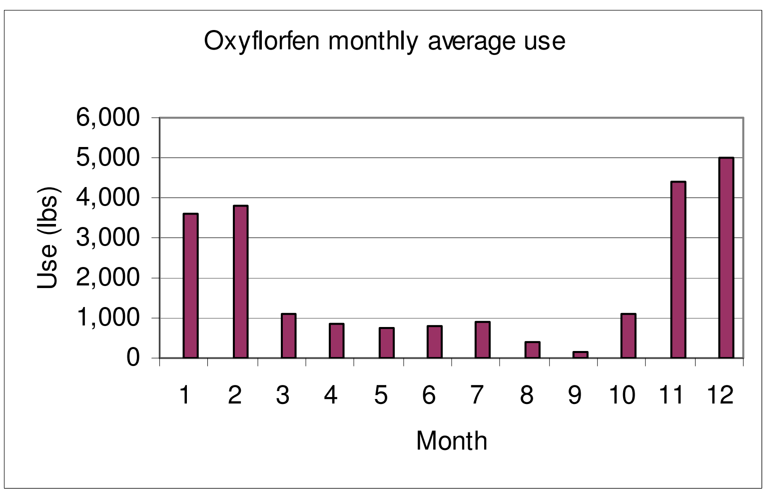


Figure Oxyfluorfen.2



Paraquat dichloride
Uses: Herbicide.

Physical properties: Paraquat dichloride has very high water solubility (626,000 mg/L), very high Koc (10,000), and very long half-life in soil (620 days).

Toxicity: The 96-hour LC_{50} ranges from 11,000 to 156,000 µg/L, and the most sensitive species is Scud (*Gammarus fasciatus*). The EC50 ranges from 0.55 to 50,000 µg/L tested on aquatic plants between 96 hours and 14 days. The lowest EC50 value was from a 96-hour test on freshwater diatom (*Navicula pelliculosa*).

Water quality criteria: no WQC is proposed.

Usage: The average annual use was 40,268 lbs with the highest use of 56,685 lbs in 1996 and the lowest use of 25,966 lbs in 2001 (Figure Paraquat.1). Paraquat dichloride was used almost year-round, but relatively higher uses were from January to May and lower uses were between July and November (Figure Paraquat.2).

The major crops to which paraquat dichloride is applied are alfalfa (21%), almond (19%), pear (9%), and prune (7%).

The average annual area of application was 53,142 acres.

Water quality data: There are no concentration data available for paraquat dichloride in the DPR SWDB.

Conclusion: Paraquat dichloride is ranked as high risk because of its high toxicity to aquatic plants and application time (winter season). However, the risk may be lower because the annual uses have been decreased. Paraquat dichloride is an herbicide, so it is highly toxic to aquatic plants but slightly toxic to aquatic animals. Sediment contamination is potential because of its high Koc and long half-life in soil.

Figure Paraquat.1

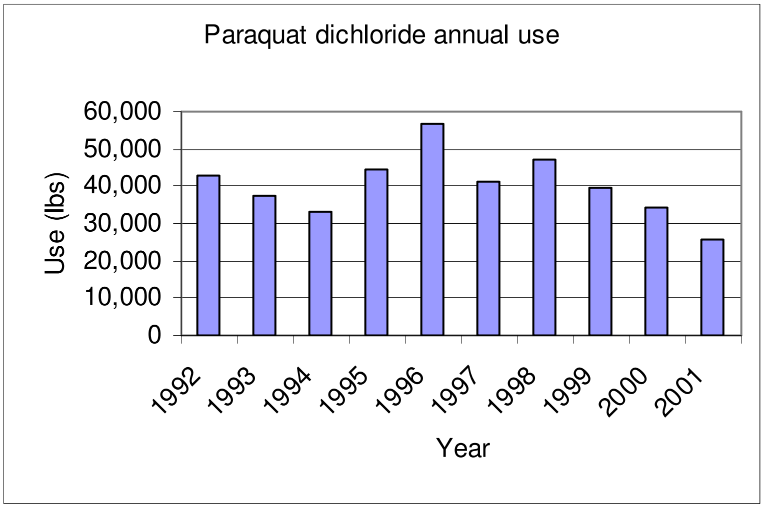
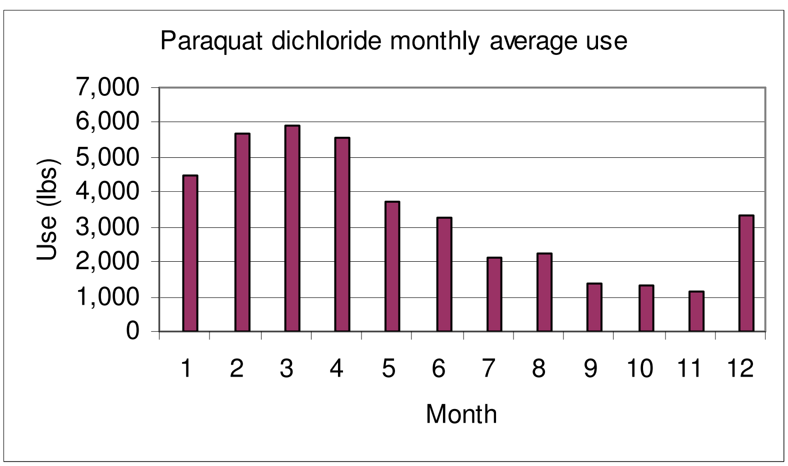


Figure Paraquat.2



Permethrin
Uses: Insecticide, one of the pyrethroid family.

Physical properties: Like other pyrethroid insecticides, permethrin has very low water solubility (0.006 mg/L), very high Koc (100,000), and short half-life in soil (30 days).

Toxicity: The EPA toxicity database has 96-hour LC_{50} from 0.018 to 536 µg/L. The most sensitive species was stone crab larvae (*Menippe mercenaria*).

Water quality criteria: The CDFG has proposed interim freshwater quality CCC (0.059 µg/L) and CMC (0.03 µg/L) values. The most sensitive species for acute tests was the mayfly (*Hexagenia bilineata*) with a GMAV of 0.10 µg/L.

Usage: The annual use of permethrin has decreased from 1998 to 2001 with an average of 16,005 lbs. The highest annual use was 20,277 lbs in 1992 and the lowest use was 10,967 lbs in 2001 (Figure Permethrin.1). The amount of permethrin reportedly used in 2001 was about 54% of the amount used in 1992. The monthly use pattern shows that the highest uses were from May to August with the highest use in June (Figure Permethrin.2). There were some uses in January and March but very low uses in February.

The average area on which permethrin was used from 1992 to 2001 was 76,128 acres.

The major crops to which permethrin is applied include peach (40%), walnut (20%), almond (13%), alfalfa (10%), pistachio (4%), and corn (4%). The major applications were in January and February on almond and peach. In March and April, heavy uses were on alfalfa and corn. The highest monthly use was in June on peach. In general, the total of amount of use in summer was higher than in winter.

Water quality data: There are 76 concentration data points in the DPR SWDB, but none exceeded the LOQ (0.005 µg/L). The data were collected from the Sacramento River watershed from 1996 to 1998.

Conclusion: Permethrin is ranked as high risk because of its very high toxicity. The risk to surface water could be lower because permethrin has very low water solubility, relatively decreased uses reported in recent years, and no concentrations were detected in the surface water. However, permethrin, like all other pyrethroid compounds, has high Koc and low half-life in soils that indicate high potential risk for sediment contamination.

Figure Permethrin.1

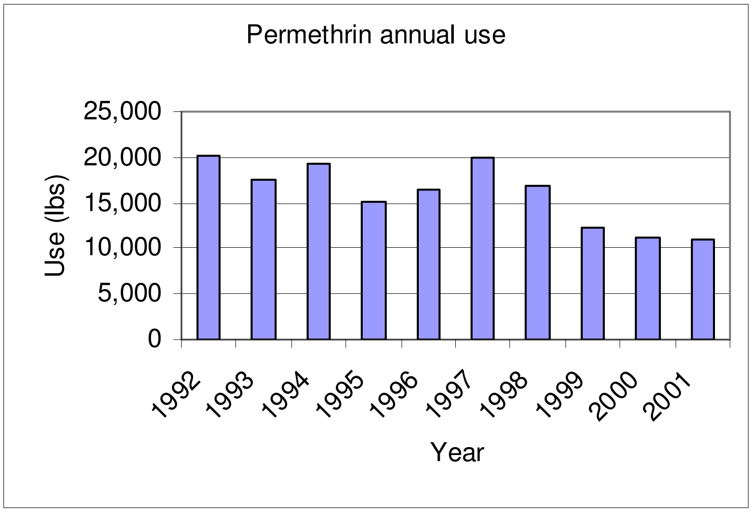
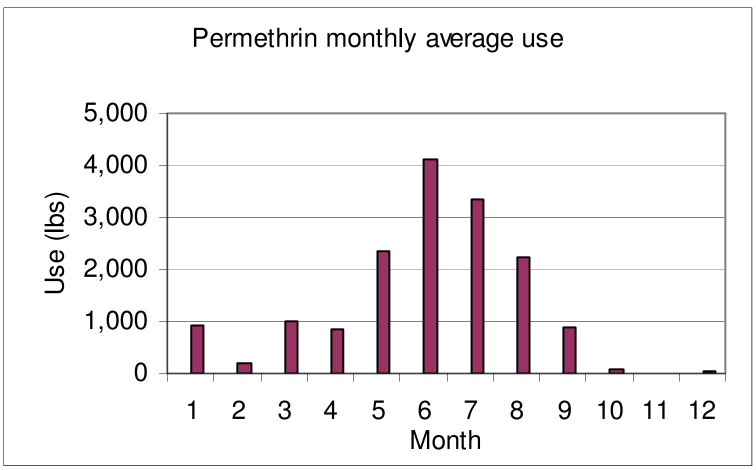


Figure Permethrin.2



Propanil
Uses: Herbicide.

Physical properties: Propanil has high water solubility (200 mg/L), moderate Koc (149), and very low half-life in soil (less than one day).

Toxicity: The 96-hour LC_{50} ranges 400 to 16,000 µg/L tested on aquatic animals and the most sensitive species is a mysid (*Mysidopsis bahia*). The EC50 ranges from 16 to 110 µg/L tested on aquatic plants between 5 and 14 days. The lowest EC50 value was from a 5-day test on freshwater diatom (*Novicula pelliculosa*).

Water quality criteria: no WQC is proposed

Usage: The average annual use was 413,503 lbs from 1992 to 2001. The highest use was 1,340,413 lbs in 2001 that was about 100 time of the amount used in 1992 (Figure Propanil.1). The annual use increased rapidly from 1998 to 2001 with the increase rate in 39% per year. The annual use was 977,942 lbs from 1998 to 2001. The monthly use shows the highest use in May (Figure Propanil.2). There were no uses between September and January.

The average annual area to which propanil was applied was 100,070 acres. Since the high increase in use between 1998 and 2001, the average annual acreage use also was increased to 236,871 acres.

Over 99% of the propanil was applied on rice.

Water quality data: The highest concentration (20.6 µg/L) was detected in May 2001 (Figures Propanil.3 and Propanil.4). The high use amounts in May apparently resulted in the high concentration. The highest concentration is far below the lowest LC_{50} (400 µg/L) tested on aquatic animals but higher than the lowest EC50 (16 µg/L) tested on aquatic plants.

Conclusion: Propanil is ranked as high risk because it has high toxicity to aquatic plant and the amount of annual use has been increased in recent years. Propanil is an herbicide used on rice. It is highly toxic to aquatic plant but moderately toxic to aquatic animals. The risk to sediment is possible because propanil has moderate Koc and the short half-life in soil.

Figure Propanil.1

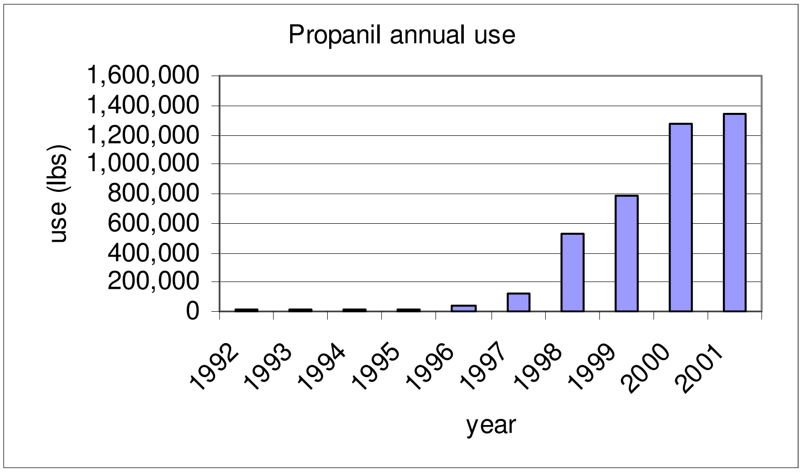


Figure Propanil.2

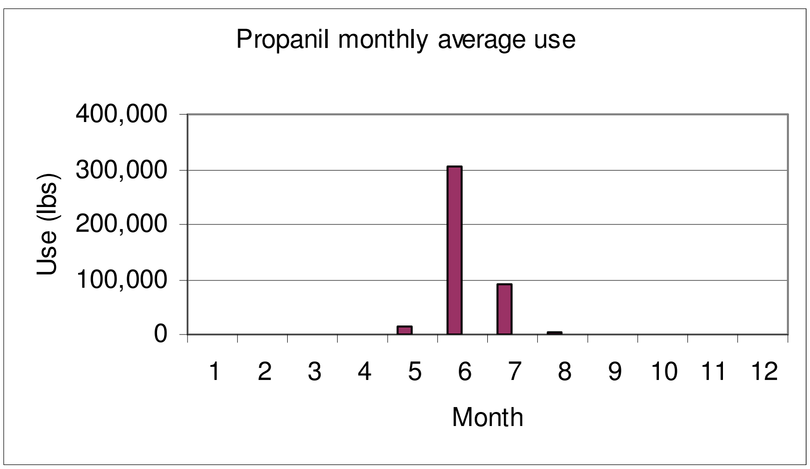


Figure Propanil.3 (zero indicates the concentration below detection limit)

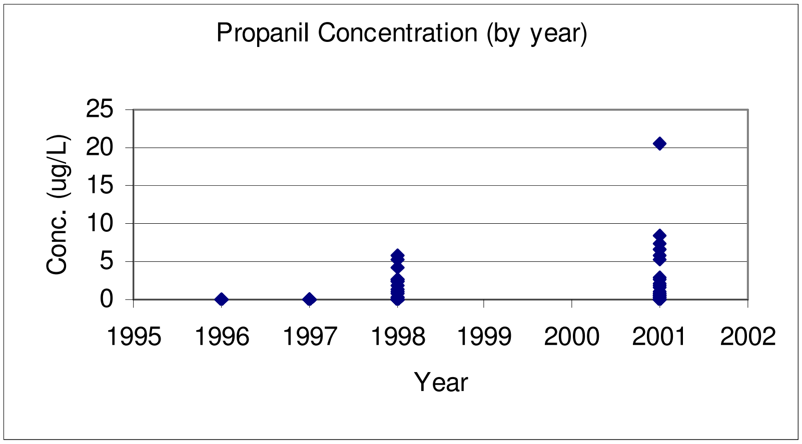
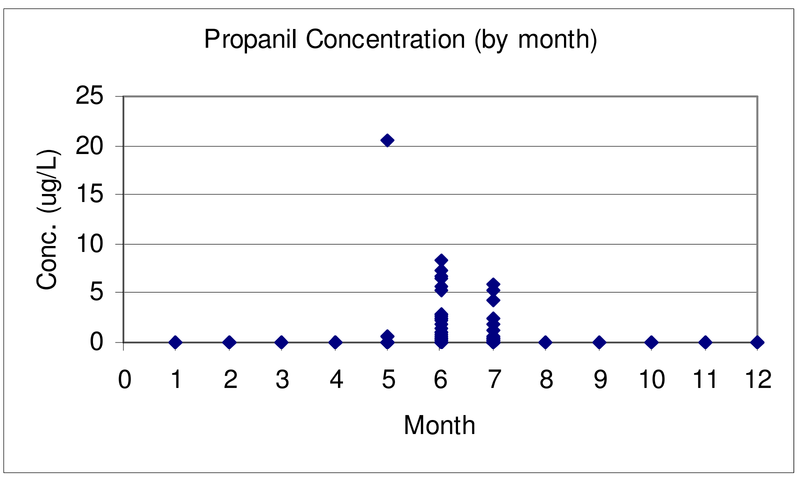


Figure Propanil.4



Propargite
Uses: Insecticide.

Physical properties: Propargite has very low solubility (0.5 mg/L), high Koc (4,000), and moderate half-life in soil (56 days).

Toxicity: The 96-hour LC_{50} ranged from 31 to 3,700 µg/L. The most sensitive species was bluegill sunfish (*Lepomis macrochirus*).

Water quality criteria: no WQC are proposed.

Usage: The average annual propargite use was 94,245 lbs from 1992 to 2001. The highest use was in 1997 and the lowest use was in 1993 (Figure Propargite.1). The amount of use increased from 1998 to 2001. The amount used in 2001 was about 147% of the amount used in 1999. The months of heavy use are from June to August with the highest use in July (Figure Propargite.2). There were almost no applications of propargite in the winter.

The average annual area to which propargite was applied was 56,376 acres.

Propargite was reportedly applied on almond (24%), walnut (21%), beans (14%), and corn (12%).

Water quality data: The DPR SWDB has 76 propargite concentration data. The water samples were collected from November 1996 to August 1998. Only one sample exceeded LOQ (0.013 µg/L) and it was 0.0523 µg/L observed in May 1997.

Conclusion: Propargite is ranked as high risk because of its high toxicity and increased amount of use. The risk could be lower if only considering the concentration in water because it is almost insoluble in water. The risk could also be lower for the storm season because of almost no use in winters. However, there is a potential risk for sediment contamination because of its high Koc and moderate half-life in soil.

Figure Propargite.1

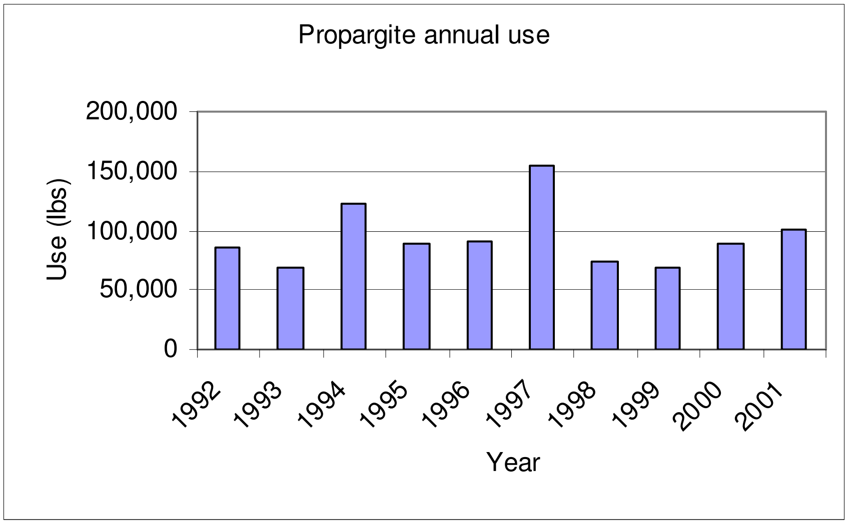
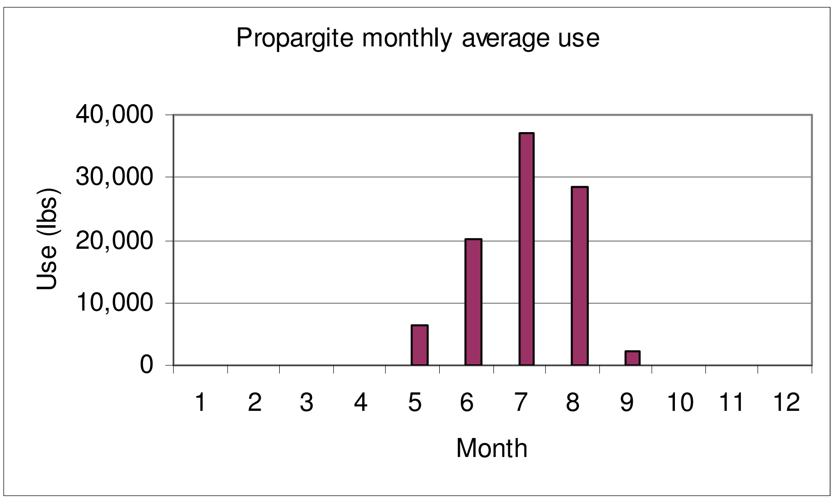


Figure Propargite.2



Thiobencarb
Uses: Herbicide used on rice fields.

Physical properties: Thiobencarb has relatively low water solubility (28 mg/L), moderate Koc (900), and low half-life in soil (21 days).

Toxicity: The 96-hour LC_{50} ranges from 150 to 2,540 µg/L, and the most sensitive species is a mysid (*Mysidopsis bahia*). The EC50 ranges from 17 to 3,100 µg/L tested on aquatic plants between 4 and 14 days. The lowest EC50 value was from a 5-day test on green algae (*Selenastrum capricornutum*).

Water quality criteria: Thiobencarb is applied to rice fields along with molinate, therefore, the criteria were determined considering the effects of both herbicides. The CDFG proposed water quality criterion for thiobencarb is 3.1 µg/L (CDFG, 1990).

Usage: The average annual use is 582,310 lbs from 1992 to 2001. The highest annual amount used was 974,766 lbs in 2000 and the lowest use was 180,129 lbs in 1992 (Figure Thiobencarb.1). General speaking, the amounts of use increased during the 10 year period. The amount of use in 2000 was over five times the amounts used in 1992, but the amount of use has decreased from 2000 to 2001. The highest use of thiobencarb was in May and second high use was in June (Figure Thiobencarb.2).

Thiobencarb is used only on rice fields.

The average annual area to which thiobencarb is applied is 144,587 acres.

Water quality data: Over one thousand samples with thiobencarb concentration data are recorded in the DPR SWDB. The highest thiobencarb concentration (16.9 µg/L) is higher than the CDFG-recommended value (3.1 µg/L). The high concentrations were observed in May and June from 1996 to 2002.

Conclusion: Thiobencarb is ranked as high risk because of its high toxicity and increased amount of use in recent years. This herbicide has drawn great attention for decades (SWRCB, 1984). Detailed studies have been done for many years and regulations have been enforced to reduce the amount of thiobencarb detected in surface water. Sediment contamination is possible based on the value of Koc and soil half-life.

Figure Thiobencarb.1

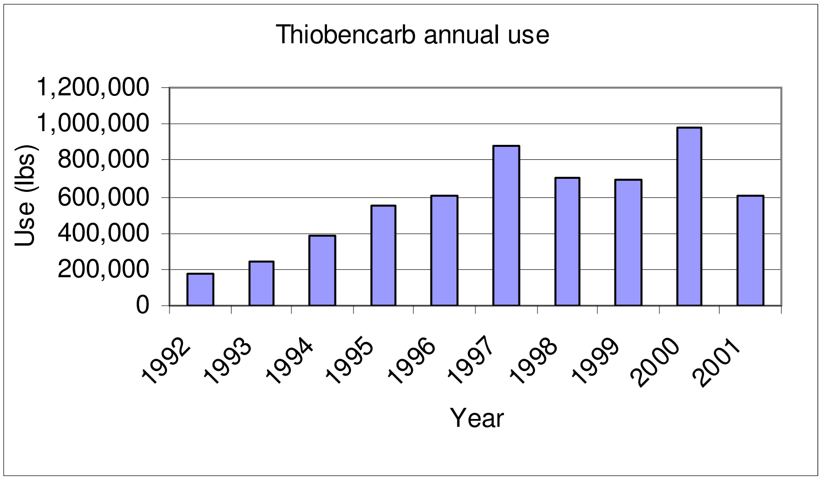


Figure Thiobencarb.2

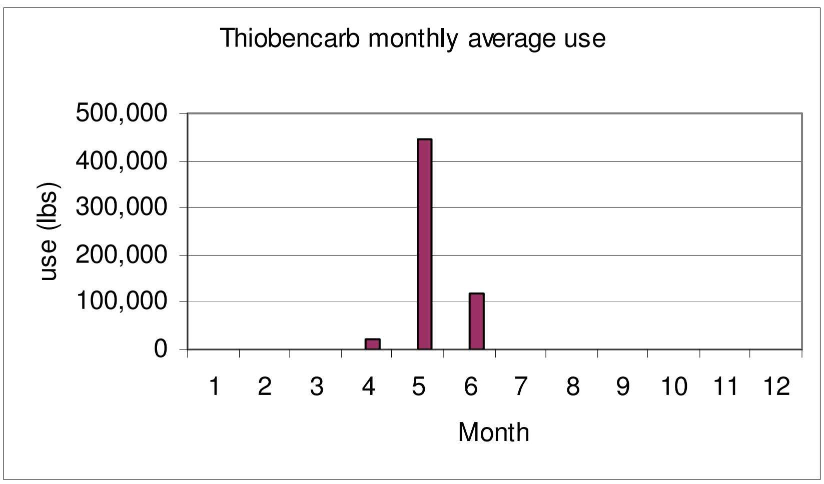


Figure Thiobencarb.3 (zero indicates the concentration below detection limit)

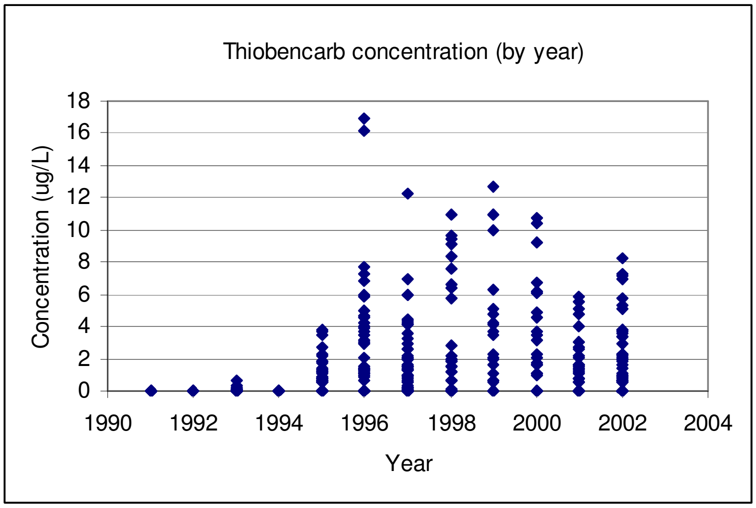
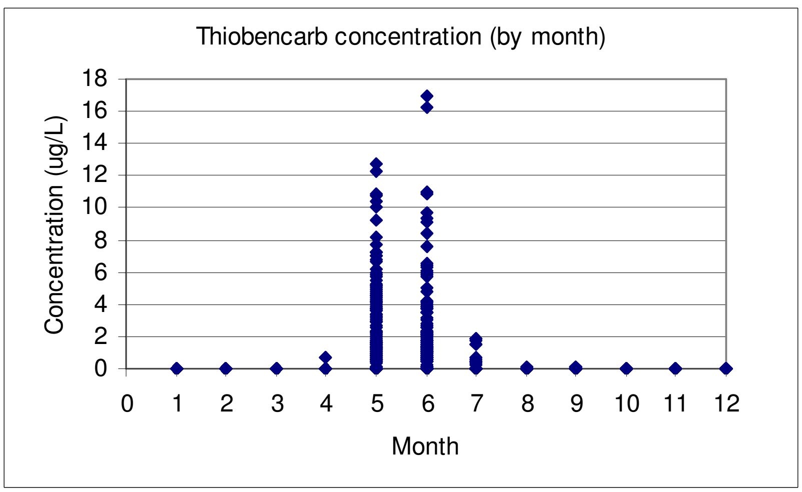


Figure Thiobencarb.4



Trifluralin
Uses: Herbicide.

Physical properties: Trifluralin has very low water solubility (0.3 mg/L), high Koc (8,000), and moderately long half-life in soil (60 days).

Toxicity: The 96-hour LC_{50} ranges from 8.4 to 22,000 µg/L for fishes and crustaceans. The most sensitive species is the bluegill sunfish (*Lepomis macrochirus*). The EC50 ranges from 15.3 to 5,000 µg/L tested on aquatic plants between 5 and 14 days. The lowest EC50 value was from a 5-day test on freshwater diatom (*Navicula pelliculosa*).

Water quality criteria: no WQC or goals were proposed.

Usage: The average annual use 54,285 lbs (after removal of one record that was for sugarbeet at application rate of 3,090 lb/acre for 27 acres). The annual uses were gradually decreased between 1992 and 2001 with the highest use in 1992 and lowest use in 2001 (Figure Trifluralin.1). The amount of use in 2001 was 49% of the amount used in 1992. Trifluralin was applied year round but the high amounts of use were from January to June and the highest uses were in April and May (Figure Trifluralin.2).

The major crops to which trifluralin is applied are tomatoes (23%), alfalfa (25%), safflower (19%), and beans (4%).

The average annual area to which trifluralin is applied is 66,453 acres.

Water quality data: The DPR SWDB has 940 samples with trifluralin data and the highest concentration was 0.023 µg/L observed in February 1994 (Figures Trifluralin.3 and Trifluralin.4). The observed highest concentration was much lower than the toxicity data on aquatic plants

Conclusion: Trifluralin is ranked as high risk because of its high toxicity and application time (winter storm season applications). The risk may be lower because the annual uses were reduced in recent years. In addition, no observed concentrations in the surface water exceeded the lowest toxicity. The risk for sediment contamination is high because trifluralin has high Koc and moderate half-life in soil.

Figure Trifluralin.1

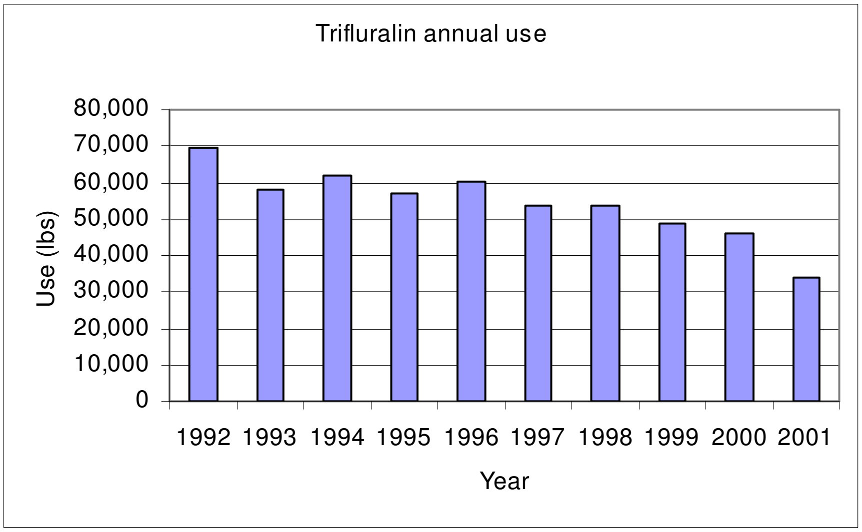


Figure Trifluralin.2

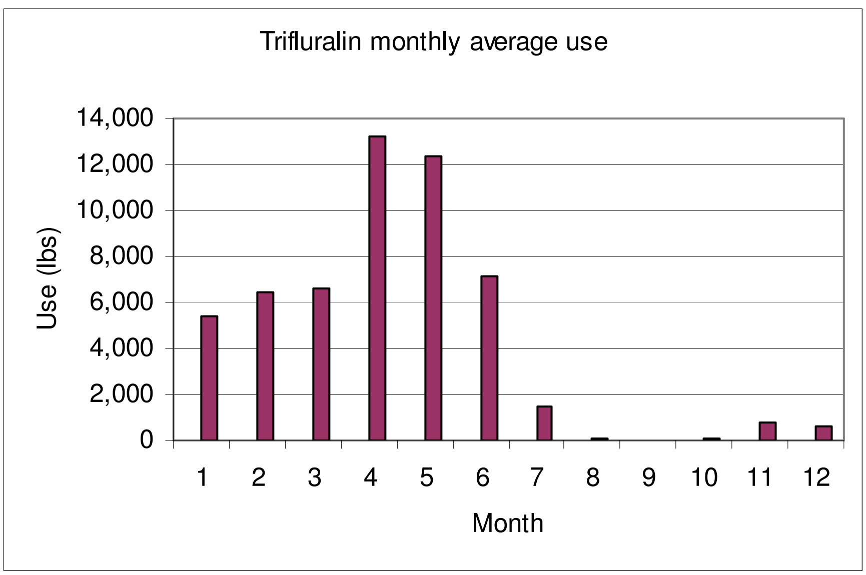


Figure Trifluralin.3 (zero indicates the concentration below detection limit)

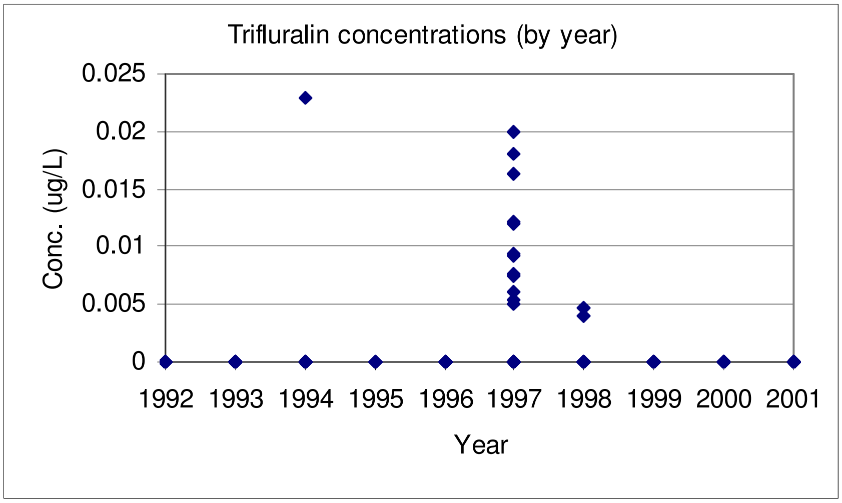
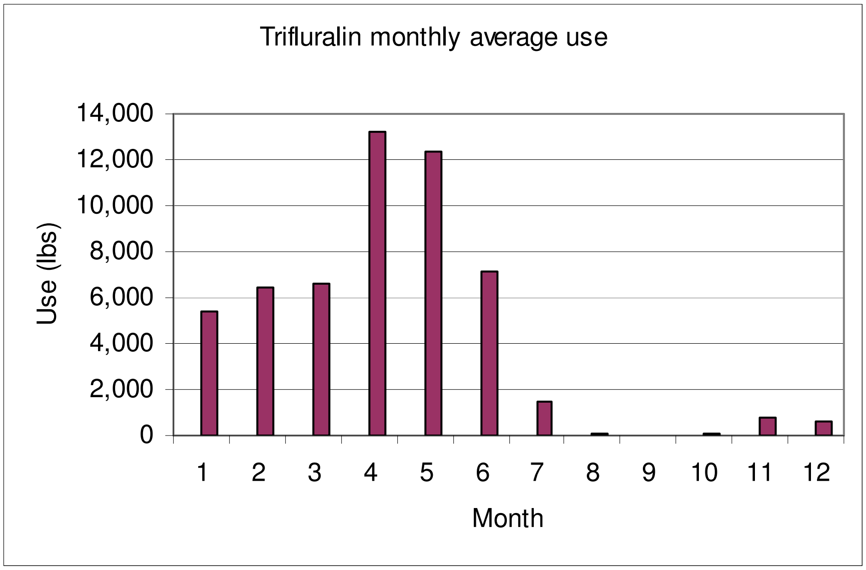


Figure Trifluralin.4



Ziram
Uses: Fungicide.

Physical properties: Ziram has moderate solubility (65 mg/L), moderate Koc (400), and low half-life in soil (30 days). The hydrolysis varies with pH, ranging from minutes to several days.

Toxicity: The 96-hour LC_{50} ranges from 8 to 1,700 µg/L. The most sensitive species was the fathead minnow (*Pimephales promelas).*

Water quality criteria: The CDFG had a report about the hazard assessment for aquatic organisms but no WQC were determined because of insufficient data. The genus mean acute value (GMAV) is 9.7 µg/L on sunfish (*Lepomis macrochirus*).

Usage: The annual use of ziram ranged from 163,768 to 595,873 lbs from 1992 to 2001. The highest use was in 1995 and the lowest use was in 2000 (Figure Ziram.1). The reduction was 73%. The amount of use has decreased but the decrease was not consistent, such as the amounts of use in 1998 and 2001 were higher than in previous years (Figure Ziram.2).

High applications of ziram were reported for the period between February and April. The highest use was in March. From June to October, the amounts reportedly applied were very low.

The major crops on which ziram is applied are almond (70%), peach (20%), and pear (7%) orchards.

The average annual application area was 77,114 acres.

Water quality data: The DPR SWDB does not have concentration data for ziram.

Conclusion: Ziram is ranked as high risk for surface water quality because of its high toxicity and winter runoff potential. The decrease of ziram use may reduce the risk but the decrease was not consistent. Ziram may cause sediment contamination because of its moderate Koc.

Figure Ziram.1

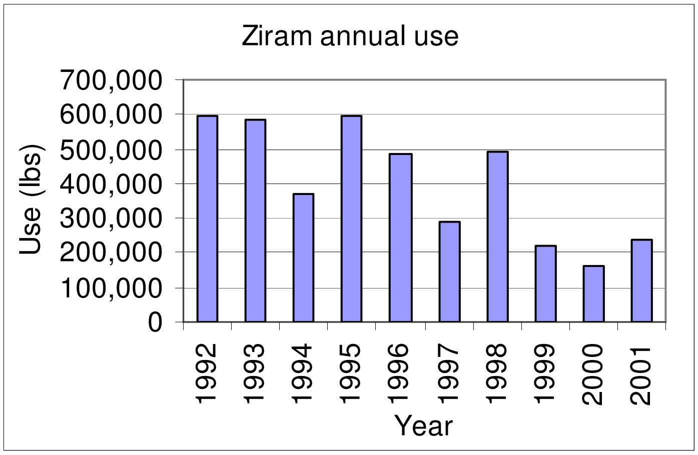
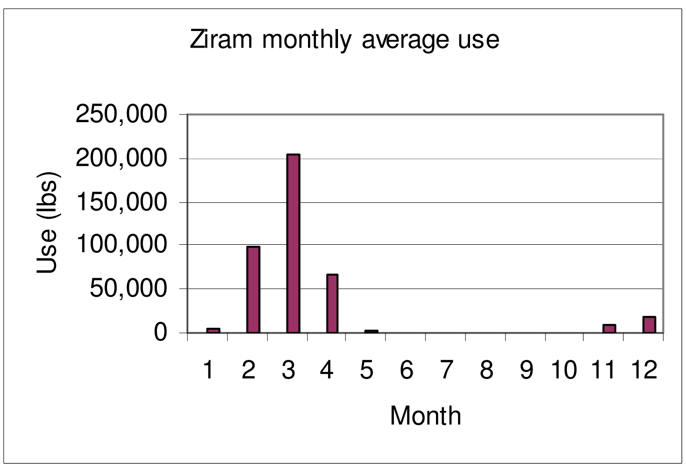


Figure Ziram.2



Appendix B. Moderate Relative Risk Pesticides

1,3-Dichloropropene
Uses: Fumigant and nematicide.

Physical properties: 1,3-dichloropropene has very high water solubility (2,250 mg/L), low Koc (32), and low half-life in soils (10 days).

Toxicity: The 96-hour LC_{50} ranges from 640 to 7,090 µg/L. The lowest 96-hour LC50 value was tested on mysid (*Mysidopsis bahia*). The lowest 48-hour LC_{50} is 90 µg/L for the water flea (*Daphnia magna*).

Water quality criteria: no WQC is proposed.

Usage: The average annual use was 12,528 lbs between 1993 and 2001. There were no reported uses in 1992 and between 1994 and 1996. The highest use was 275,759 lbs in 2001 and the lowest use was 322 lbs in 1993 (Figure 1,3 Dichloropropene.1). From 1997, the amount of use increased. The monthly uses showed that the relatively high uses were in October and November (Figure 1.3 Dichloropropene. 2).

The major reported applications are to peach (28%), prune (22%), and walnut orchards (20%), and soil preparation for planting (10%).

During the ten-year period (1992 –2001), no 1,3-dichloropropene was applied between 1994 and 1996, so the total application acreage was 2,858 acres and the average annual application was 476 acres.

Water quality data: There are no 1,3-dichloropropene water column concentration data in the SWDB.

Conclusion: 1,3-dichloropropene is ranked as a moderate risk because it is moderately toxic to aquatic organisms. The amount of use is increasing and it is easily dissolved in water. Since this pesticide is liquid, spillage control is very important. Gaseous applications could cause offsite movement that may contaminate surface water by direct deposition. The low Koc and low soil half-life indicate that 1,3-dichloropropene will not likely cause sediment contamination.

Figure 1,3 Dichloropropene.1

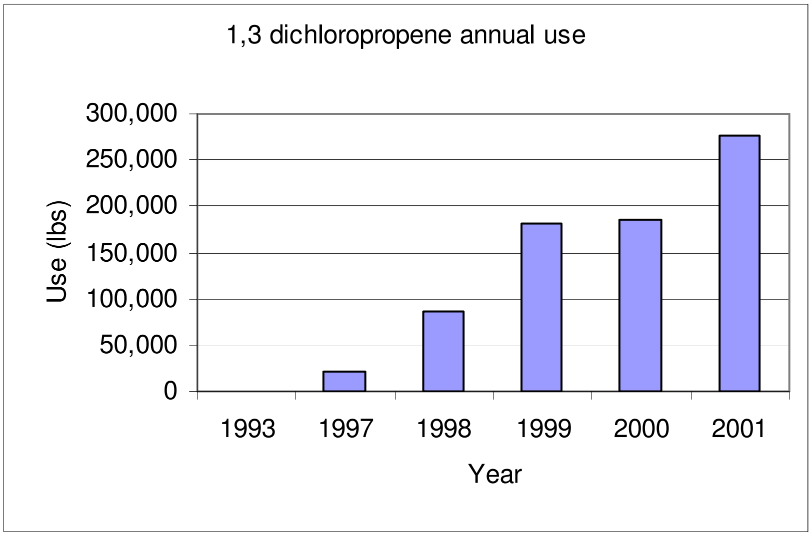
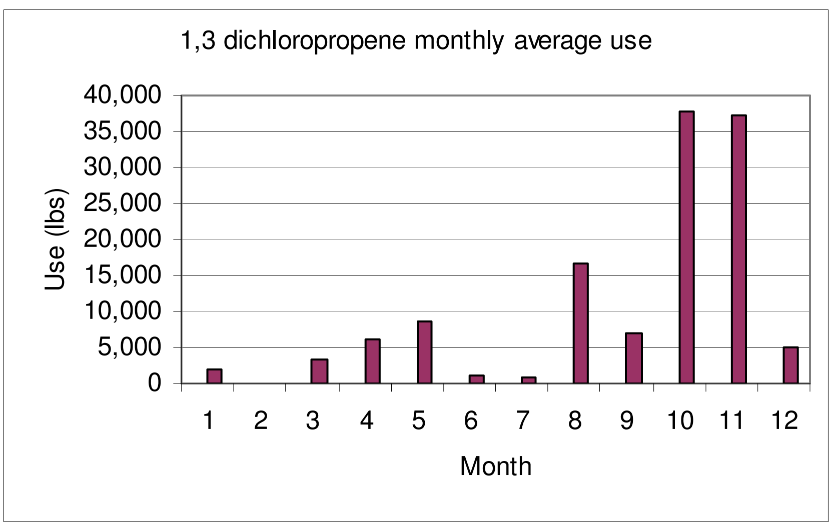


Figure 1,3 Dichloropropene.2



2,4-D, dimethylamine salt
Uses: Herbicide.

Physical properties: 2,4-D, dimethylamine salt has very high solubility (796,000 mg/L), low Koc (20), and low half-life in soil (10 days).

Toxicity: The 96-hour LC_{50} ranges from 140 to 524,000 µg/L. The lowest value was tested on grass shrimp (*Palaemonetes pugio*) and the highest value was tested on bluegill sunfish (*Lepomis macrochirus*). The EC50 values range from 580 to 188,500 µg/L tested on aquatic plants between 96 hours and 14 days. The lowest EC50 value was from a 14-day test on duckweed (*Lemina gibba*) and the lowest 5-day EC50 was 51,200 µg/L tested on green algae (*Selenastrum capricornutum*).

Water quality criteria: no WQC is proposed.

Usage: The annual amounts of 2,4-D, dimethylamine salt reportedly used ranged from 46,974 to 127,695 lbs between1992 and 2001 (Figure 2,4-D, dimethylamine.1). The lowest use was 58,314 lbs in 1999, about 37% of the amount used in 1997. In 2001, the amount of use was 70,135 lbs that was about 55% of the amount used in 1997. The monthly use distribution shows that relatively high amounts were applied before July and the highest use was in March and the lowest use was in August (Figure 2,4-D, dimethylamine.2). Relatively high amounts of used were in February and March.

The annual average area to which 2,4-D, dimethylamine salt was applied is 118,145 acres during the ten-year period from 1992 to 2001.

The major reported applications are to rice (36%), wheat (29%), and almond (9%)

Water quality data: The SWDB database has 160 concentration data points for samples collected in 1991 and 1992. None of the concentrations were over the LOQ (0.1 and 1 µg/L).

Conclusion: 2, 4-D, dimethylamine salt is ranked as a moderate risk because of its moderate toxicity to aquatic animals and the low concentrations observed in the surface waters. Even though the chemical has very high water solubility and relatively high amounts are used during the winter storm season, the observed water column concentrations were very low. 2,4-D, dimethylamine salt is an herbicide but the lowest toxicity value to aquatic plant (580 µg/L) was higher than that to aquatic animals (140 µg/L). There should be a low risk for sediment contamination because of the low Koc and the short half-life in soils.

Figure 2,4-D, dimethylamie.1

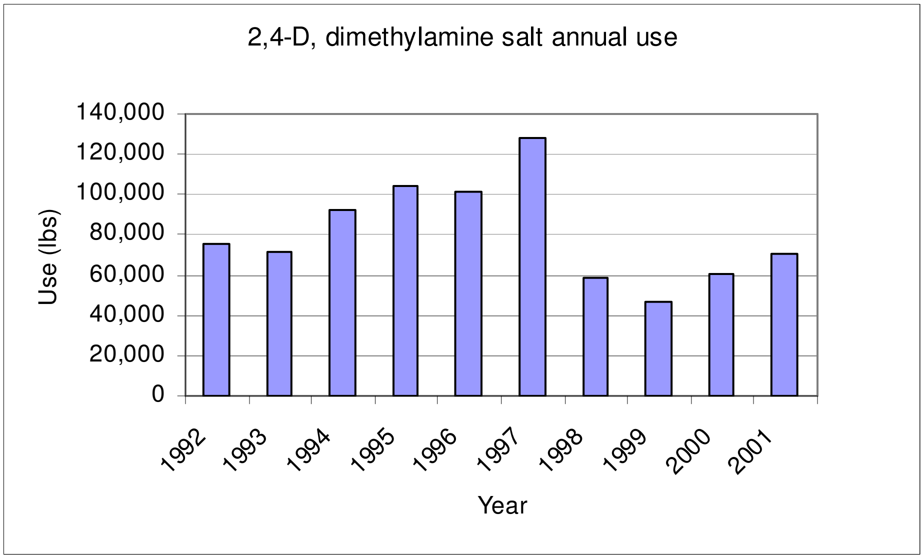
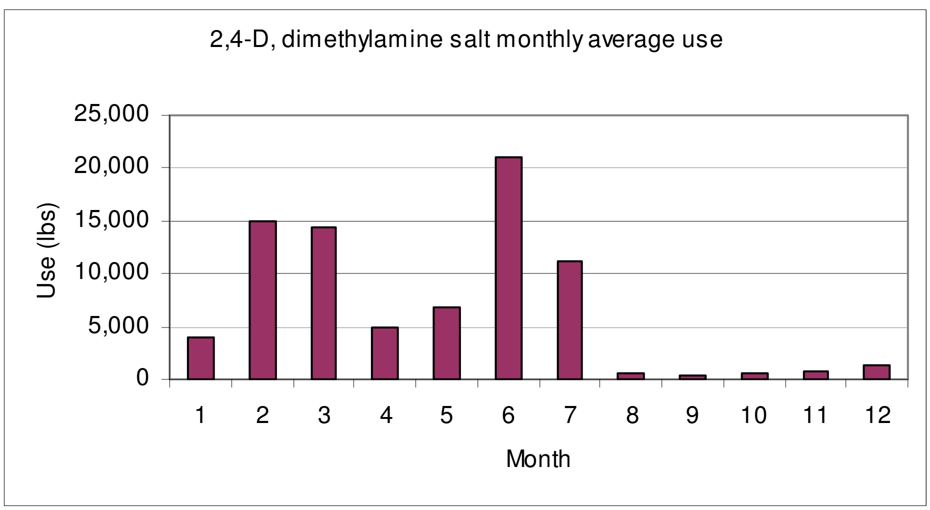


Figure 2,4-D, dimethylamie.2



Atrazine
Use: Herbicide. Atrazine was listed as the number one agricultural chemical quantities used in the US but it does not rank within the top 30 pesticides used in the Sacramento River Valley in terms of total weight and area of application.

Physical properties: Atrazine has a moderate water solubility (33 mg/L), moderate Koc (147), and long half-life in soil (173 days).

Toxicity: The 96-hour LC_{50} ranges from 4,500 to 1,000,000 μg/L for fishes and crustaceans. The lowest value was tested on rainbow trout (*Oncorhynchus mykiss*). For mysid (*Mysidopsis bahia*), the lowest 96-hour LC_{50} was 5,400 μg/L. The EC50 ranges from 22 to 460 μg/L for aquatic plants with the tested time from 2 hours to 14 days. The lowest value was tested on algae (*Isochrysis galbana*) during a 5-day test.

Water quality criteria: The instantaneous maximum advisory concentration was 1 μg/L based on the 1986 US EPA water quality advisory. The recommended maximum acute criterion (one hour average) for aquatic life protection is 1,500 μg/L according to the US EPA in 2003.

Usage: The average annual use of atrazine was 1,425 lbs from 1992 to 2001. The annual uses have generally increased from 1992 to 2001, except for 2000. The highest amount of reported use was 2,741 lbs in 2001 and the lowest use was 569 lbs in 1994 (Figure Atrazine.1). The highest uses of atrazine were in May and June (Figure Atrazine.2).

Atrazine is applied mainly on Sudan grass (69%) and corn (15%).

The annual average area of application was 761 acres.

Water quality data: There are 1,114 atrazine concentration data in the SWDB database. The highest concentration (5.3 μg/L) was detected in February 1994 (Figures Atrazine.3 and 4). Four concentration data (0.035% of total data) are over 1 μg/L and 38 data (3% of the data) are above the limit of quantitation (LOQ). All of the concentrations were much lower than the lowest 96 hour LC_{50}, the lowest 5-day EC50, and the USEPA recommended aquatic life protection acute criterion.

Conclusion: Atrazine is ranked as moderate risk because of its toxicity to aquatic plants. The risk may be increased atrazine has been found to increase the toxicity of other insecticides like chlorpyrifos. The major uses of atrazine are not during storm season, so the risk of winter storm runoff is low. Atrazine has the potential to contaminate groundwater. Sediment contamination is possible because of its relatively moderate Koc and long half-life in soil.

Figure Atrazine.1

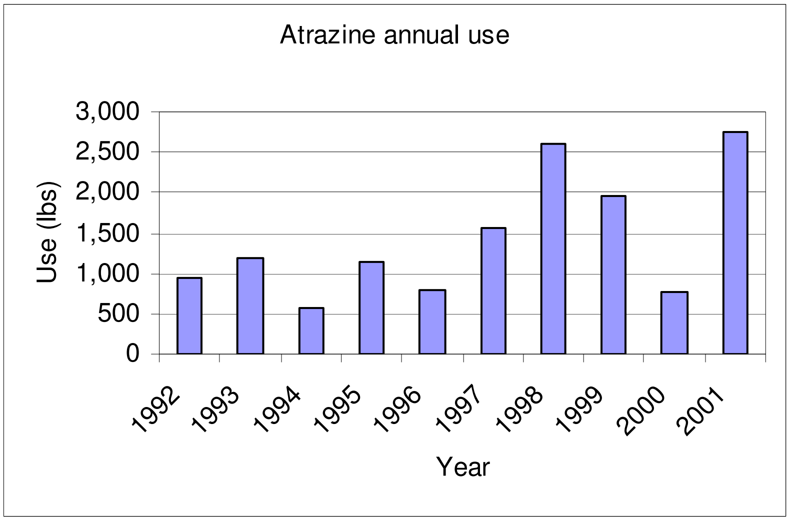


Figure Atrazine.2

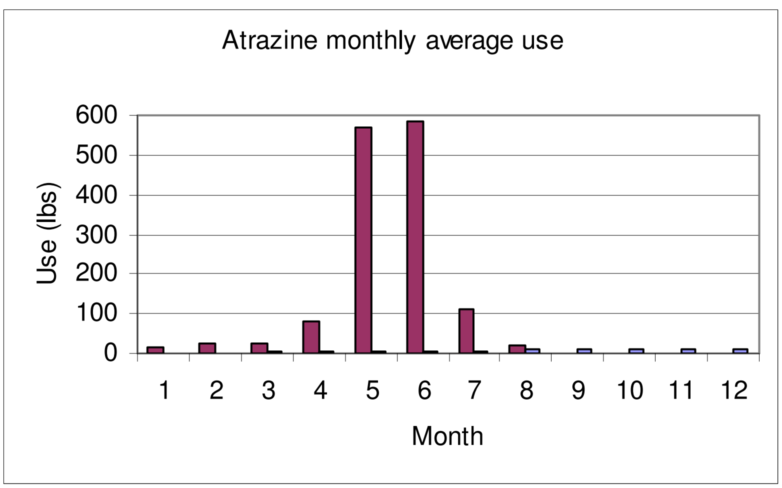


Figure Atrazine.3 (zero indicates the concentration below detection limit)

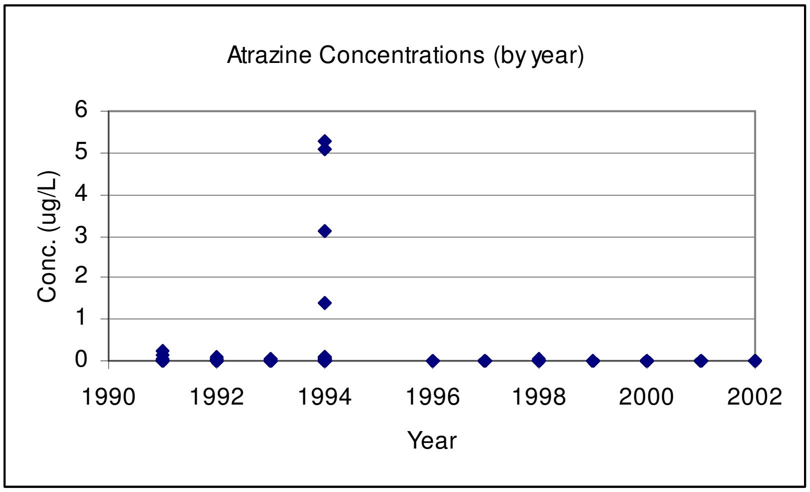
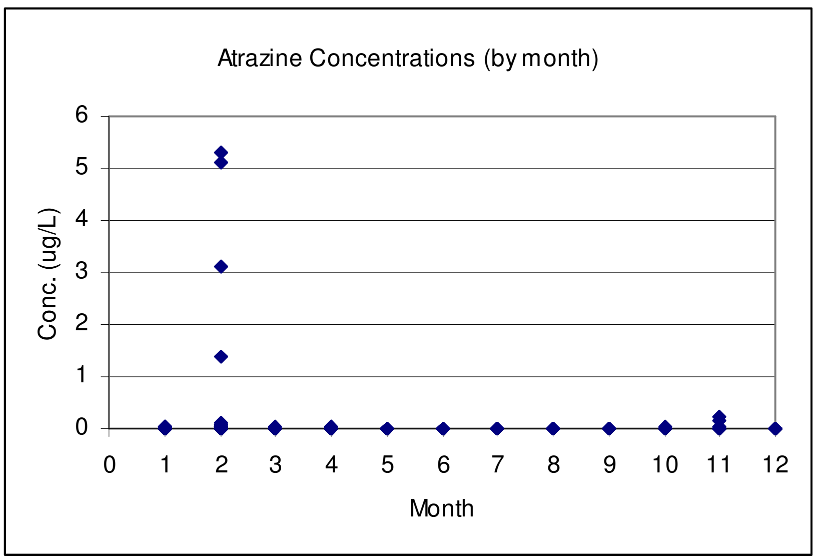


Figure Atrazine.4



Bensulfuron methyl
Uses: Herbicide.

Physical properties: Bensulfuron methyl has high water solubility (120 mg/L), moderate Koc (370), and very low half-life in soil (5 days).

Toxicity: The toxicity 96 hour LC_{50} ranges from 71,000 to 270,000 µg/L (USEPA, 2003). The most sensitive species is red crayfish (*Procambarus clarkii*). The toxicity EC50 value tested on aquatic plants has only one value (800 µg/L) that was tested on green algae (Selenastrum capricornutum) in a 128-hour test.

Water quality criteria: no WQC is proposed.

Usage: The average annual use was 75,422 lbs. The amount reportedly used between 1992 and 2001 decreased by 98%, from 263,327 to 5,505 lbs (Figure Bensulfuron methyl.1). The month of highest reported bensulfuron methyl use is May (Figure Bensulfuron methyl.2). This pesticide is mainly used on rice fields, with an average annual application of 522,982 acres.

Water quality data: There were no concentration data for bensulfuron methyl in the SWDB database.

Conclusion: Bensulfuron methyl is ranked as moderate risk because of its moderate toxicity to aquatic plants and significant reduction of reported use. Bensulfuron methyl has to be applied before rice fields are permanently flooded. The risk for sediment contamination is low because of moderate Koc and low half-life in soil.

Figure Bensulfuron methyl.1

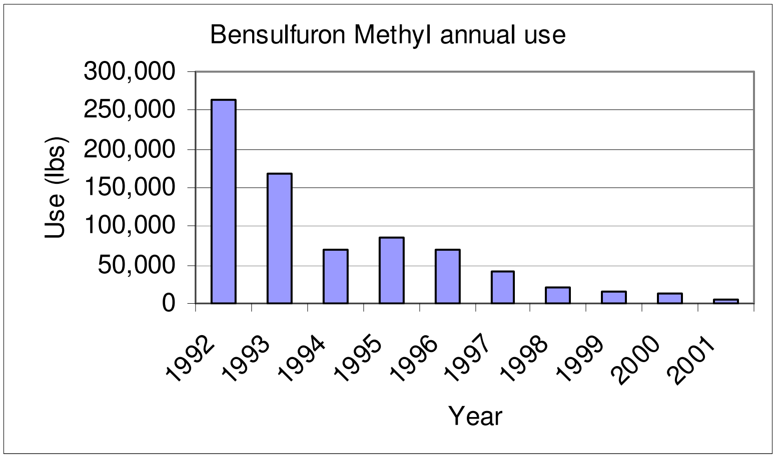
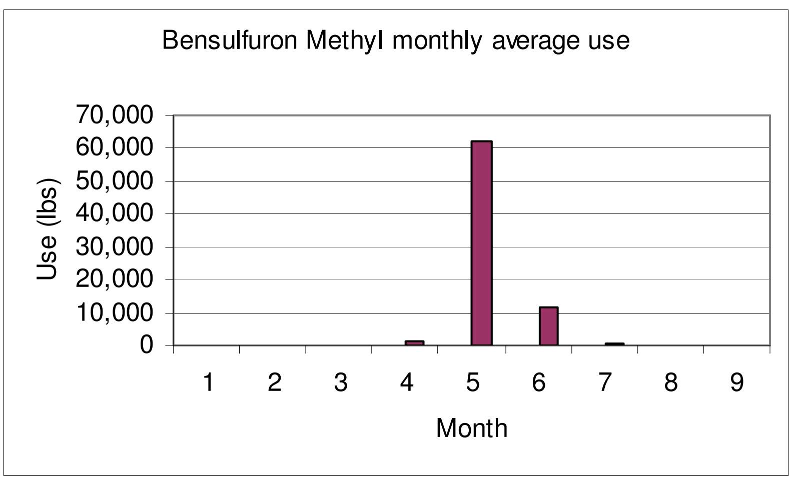


Figure Bensulfuron methyl.2



Carbaryl
Uses: Insecticide.

Physical properties: Carbaryl has a relatively high water solubility (120 mg/L), moderate Koc (300), and low half-life in soils (10 days).

Toxicity: The 96-hour LC_{50} ranged from 1.9 to 20,000 μg/L based on the EPA pesticides toxicity database (EPA, 2003). The most sensitive species was crayfish (*Procambarus sp.*).

Water quality criteria: The CDPR has reviewed the environmental fate of carbaryl. The CDFG reported a risk assessment in which the freshwater criterion of 2.53 μg/L was proposed for both the CCC and the CMC.

Usage: The annual average use was 44,358 lbs between 1992 and 2001 with the highest amount of use (83,711 lbs) in 1997 and the lowest amount of use (15,004 lbs) in 1998 (Figure Carbaryl.1). The amount of use in 2001 was 19,657 lbs, which was higher than the amount of used in 1998 but it was only 23% of the amount used in 1997. In general, the amount of use has decreased. The highest reported amount of use occurred in July and the lowest uses were in November and December (Figure Carbaryl.2). From May to August, the amount of use was relatively higher than from January to April.

The average annual area applied with carbaryl was 35,558 acres. The highest acreage was in 1997 (67,364 acres).

Carbaryl is applied on a broad rang of crops. The major crops are rice (26%), tomatoes (13%), sugarbeet (8%), peach (8%), walnut (8%), and melons (8%).

Water quality data: Hundreds of monitoring data from more than 10 sampling sites in the Sacramento River are presented in the DPR SWDB database. The highest concentration was 0.5 μg/L in May 1997 (Figures Carbaryl.3 and Carbaryl.4). It should be noticed that carbaryl was detected between October and December but very low amounts of carbaryl were applied.

Conclusion: Carbaryl is ranked as moderate risk to the surface water quality. Although it has high toxicity, the observed concentrations were lower than the lowest toxicity value and proposed CMC. However, carbaryl concentrations in surface waters were detected even with very low uses between October and December. Carbaryl may impact sediments based on its moderate Koc, but the short half-life in soil may reduce the risk level.

Figure Carbaryl.1

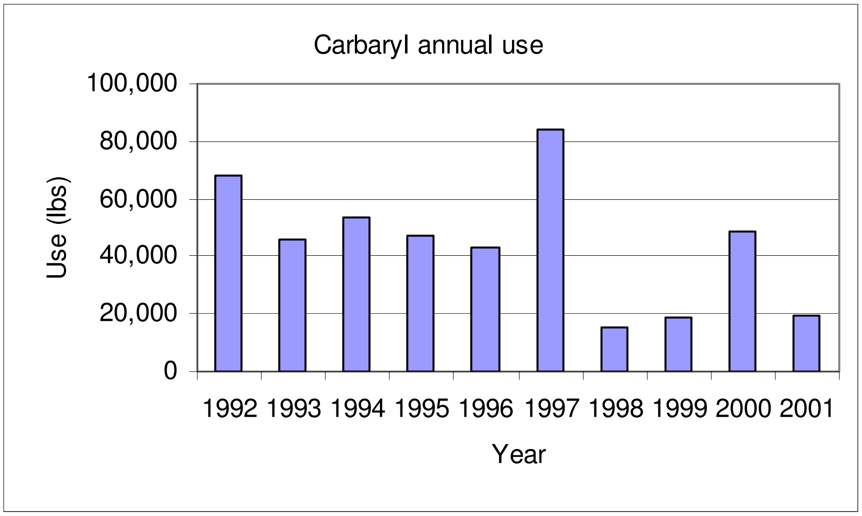


Figure Carbaryl.2

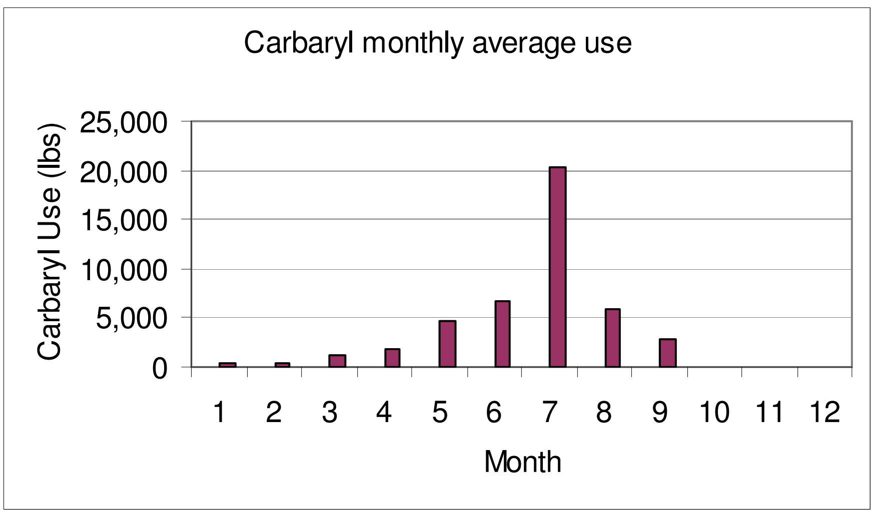


Figure Carbaryl.3 (zero indicates the concentration below detection limit)

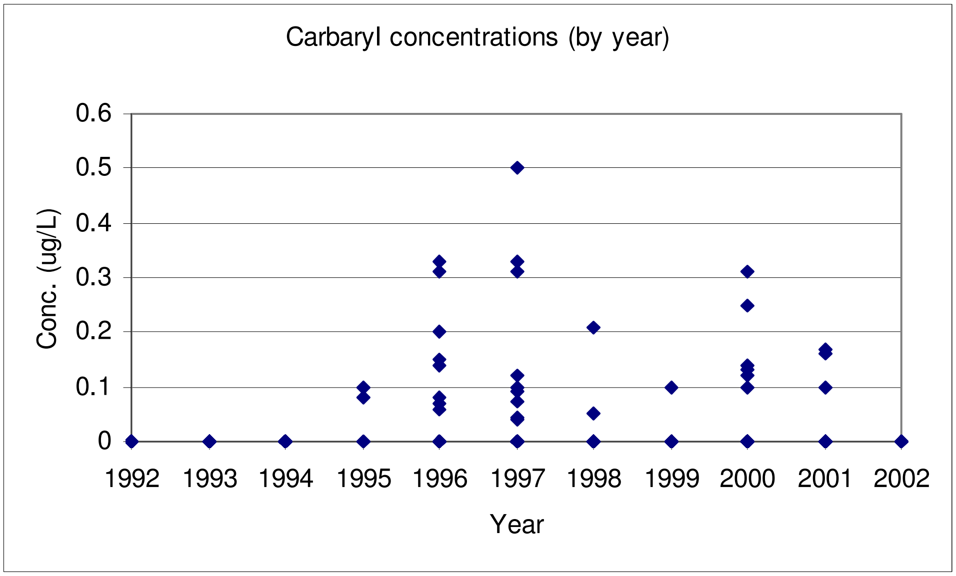
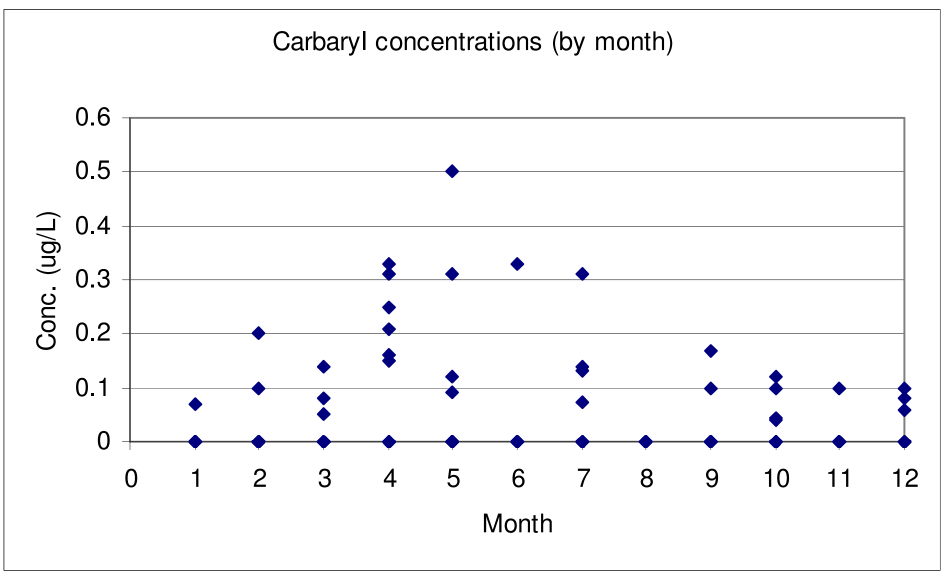


Figure Carbaryl.4



Copper oxide (ous)
Use: Fungicide.

Physical properties: Water solubility is 0.02 mg/L but no Koc and half-life values are available. Copper is strongly adsorbed to clay and humus.

Toxicity: The 96-hour LC_{50} for copper oxide was 69.7 μg/L tested on mysid (*Mysidopsis bahia*).

Water quality criteria: No WQC is determined.

Usage:
The annual use of copper oxide has decreased in recent years. The highest use of copper oxide was in 1993 and the lowest use was in 2001 with 56% decrease (Figure CopperOxide.1). The monthly average uses are showed in Figure CopperOxide.2. The highest use was in April. The amounts of used in January and May are relatively high. The major applications were on walnut, tomato, and peach. The average annual treated area was 12,088 acres.

Water quality data: No water quality data available.

Conclusion: Copper oxide (ous) is ranked as moderate risk to surface water quality because of its toxicity and decreased annual uses. Although copper oxide is used during the winter storm season to orchards, the risk of storm runoff may not be very high because copper oxide is almost insoluble in water. The annual uses of copper oxide had decreased. Koc and half-life values are not available for copper oxide (ous) but copper strongly adsorbed to soil particles, so sediment contamination is potential.

Figure CopperOxide.1

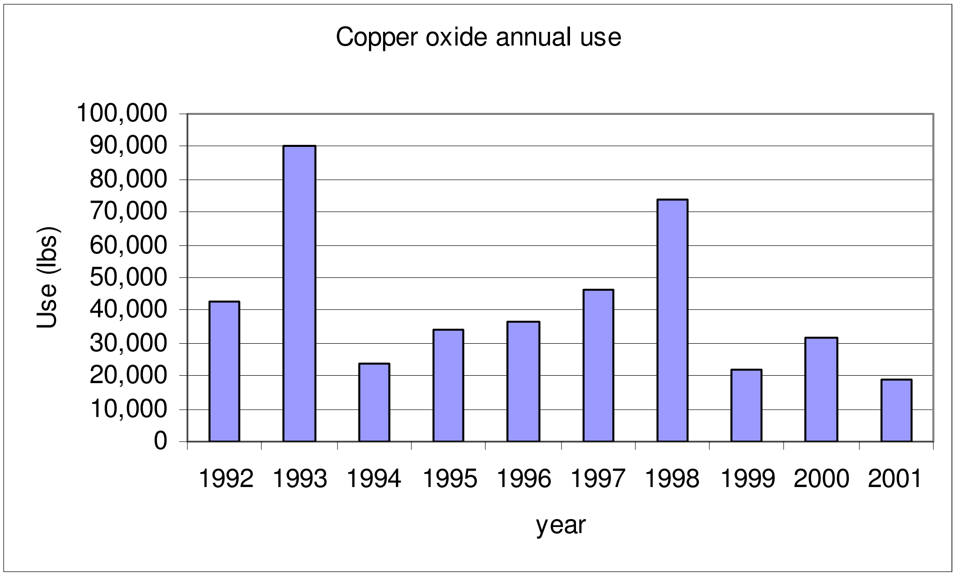
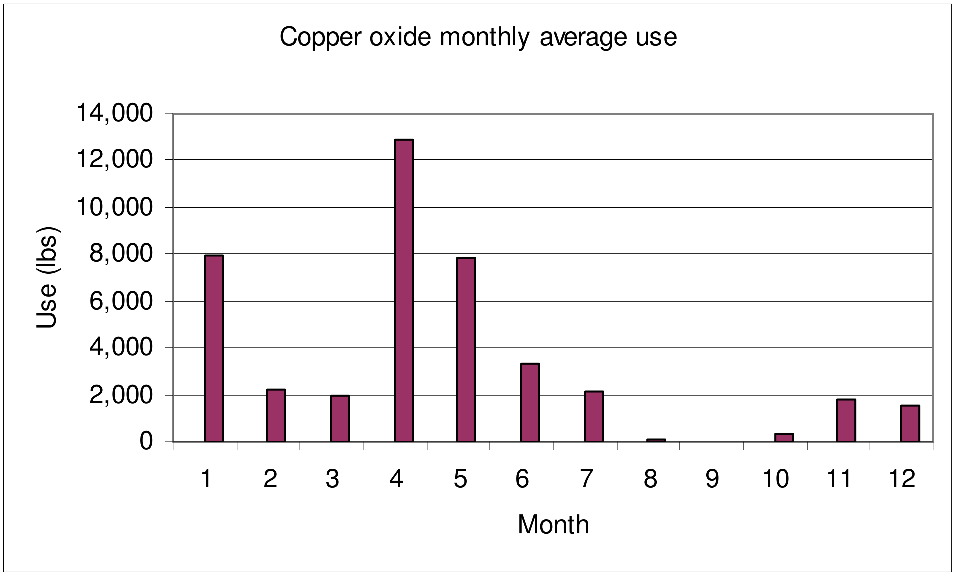


Figure CopperOxide.2



Copper sulfate (basic) and copper sulfate (pentahydrate)
Use: Fungicide.

Physical properties: no water solubility, Koc and half-life for copper sulfate are available in the ARS database. Based on EXTOXNET database, water solubility is 2,305 mg/L at 25ºC; no Koc value is available but copper is strongly adsorbed to clay and humus; and no soil half-life values are available.

Toxicity: The 96-hour LC_{50} ranges from 200 to 1,788,000 μg/L for copper sulfate (basic), the lowest value was tested on rainbow trout (*Oncorhynchus mykiss).* The 96-hour LC_{50} ranges from 130 to 28,000 μg/L for copper sulfate (pentahydrate) and the lowest value was tested on rainbow trout (*Oncorhynchus mykiss*).

Water quality criteria: No WQC is determined.

Usage:
The use of copper sulfate (basic) was increased in general except for 1999 (Figure CopperBasic.1). The highest use was 263,821 lbs in 1997 and the lowest use was 129,996 lbs in 1999. The monthly average use showed that the highest use was in January (Figure CopperBasic.2). The major crops are peach (82%), prune (13%), and almond (3%). The average annual acreage use is 15,788 acres.

The use of copper sulfate (pentahydrate) was increased in general (Figure CopperPen.1). The highest annual use was 3,140,603 lbs in 2000 and the lowest use was 1,884,733 lbs in 1993. The monthly average use shows that the highest use was in May (Figure CopperPen.2). The average annual use is 197,579 acres. The major use was on rice (96%).

Water quality data: No water quality data are available.

Conclusion: Copper sulfate (basic) and copper sulfate (pentahydrate) are ranked as moderate risk based on their toxicity values. Major amount of copper sulfate (basic) were applied during the winter storm season, the runoff could increase the risk to surface water quality. The runoff from the rice fields due to huge amount of copper sulfate (pentahydrate) used may increase the risk to surface water quality. Although no Koc and half-life values are available, copper is strongly adsorbed to soil particles, so the sediment contamination is potential.

Figure CopperBasic.1

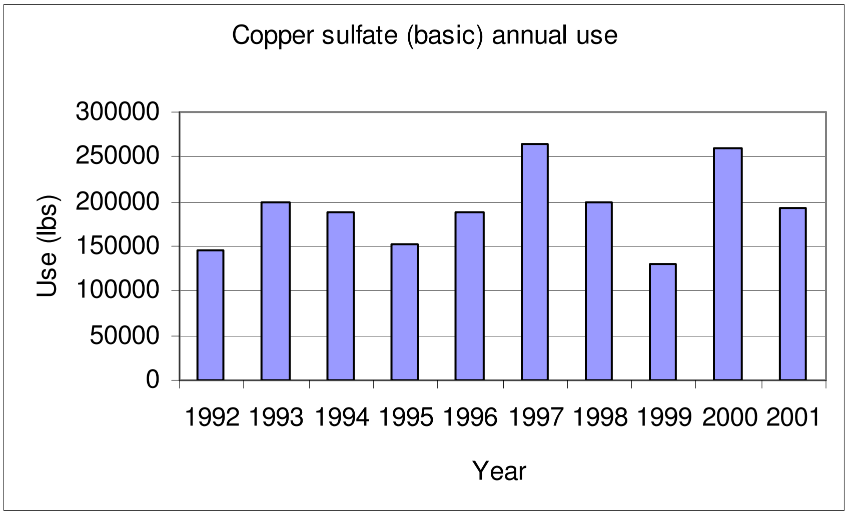


Figure CopperBasic.2

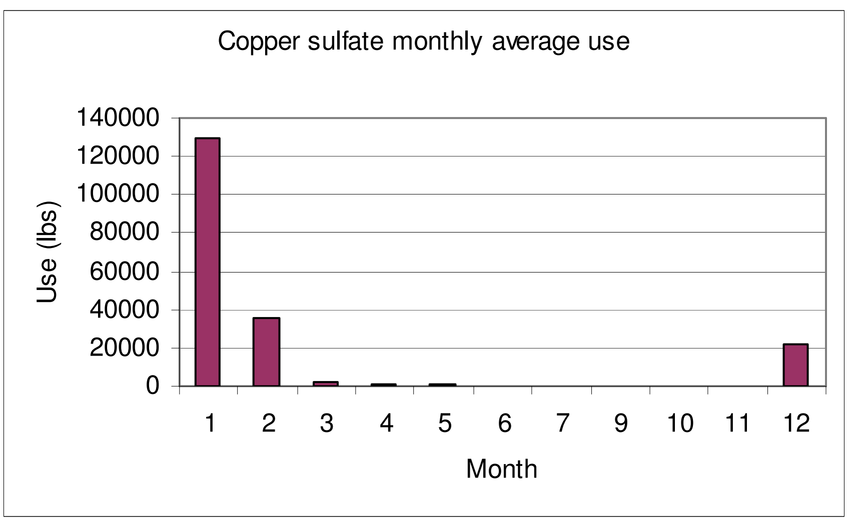


Figure CopperPen.1

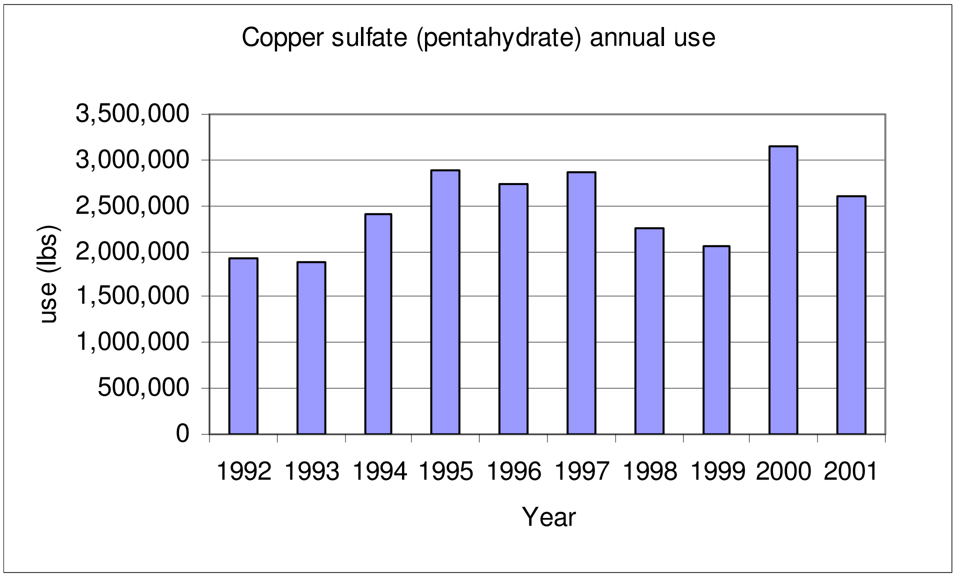
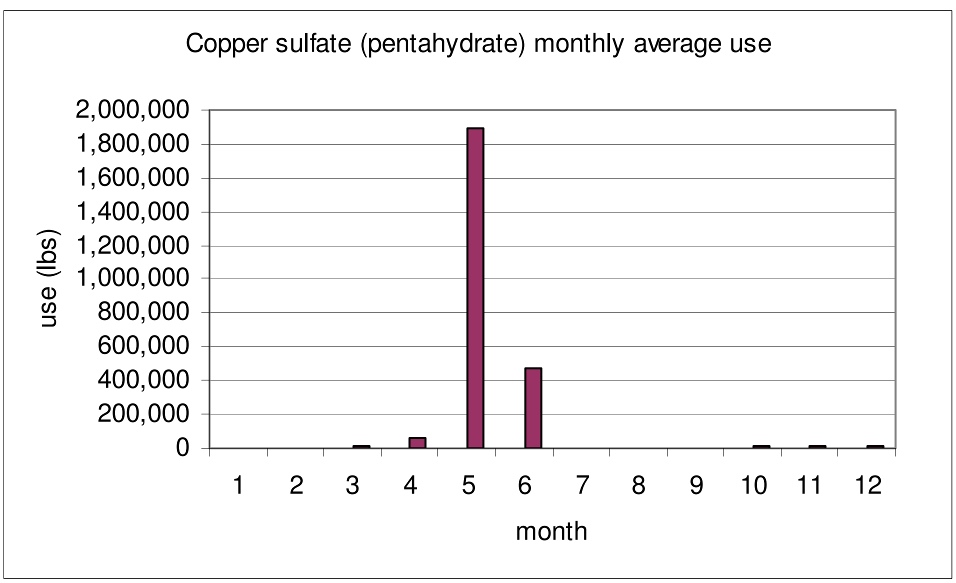


Figure CopperPen.2



Cyprodinil
Uses: Fungicide.

Physical properties: Cyprodinil has moderate water solubility (16 mg/L), high Koc (1,470), and long half-life (106 days) in soils.

Toxicity: The 96-hour LC_{50} ranges from 433 to 8,140 µg/L. The lowest value was tested on eastern oyster (*Crassostrea virginica*).

Usage: The average annual cyprodinil use was 11,843 lbs between 1998 and 2001. The annual uses increased from 1998 to 2001 with the highest use of 22,083 lbs in 2000 and the lowest use of 860 lbs in 1998 (Figure Cyprodinil.1). The monthly uses showed that the highest uses were in February and March (Figure Cyprodinil.2).

The annual average acreage was 51,313 acres.

The major applications were on orchards including 62% used on almond, 22% on prune, and 14% on peach.

Water quality data: no data available.

Conclusion: Cyprodinil is ranked as moderate risk potential for the surface water quality because of its moderate toxicity. The risk may be increased because the amount of use has increased in recent years and the application time (winter storm season). Sediment contamination risk is potential high because of its high Koc and long half-life in soils.

Figure Cyprodinil.1

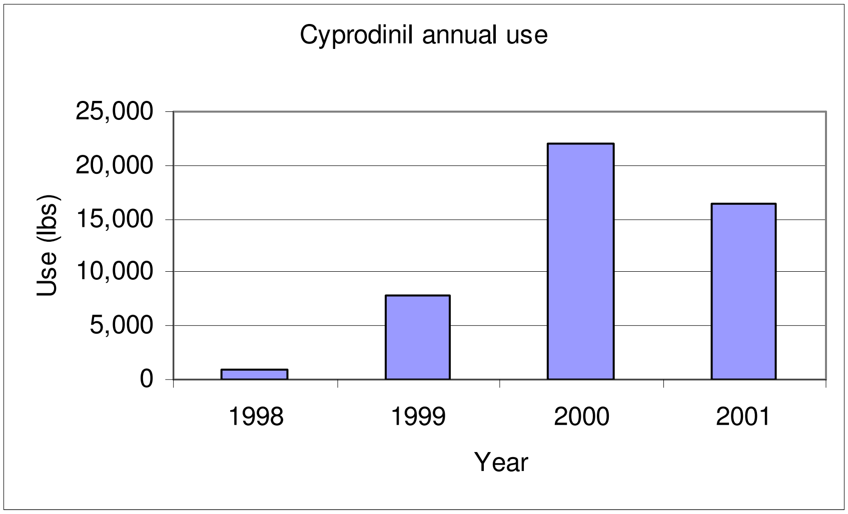
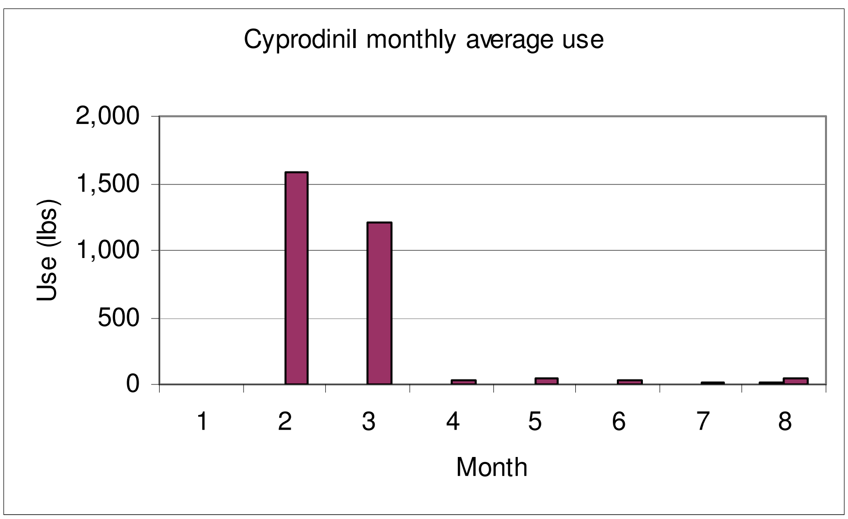


Figure Cyprodinil.2



Glyphosate-Trimesium
Uses: Herbicide.

Physical properties: Glyphosate-trimesium has very high water solubility (3,310,000 mg/L), very high Koc (24,750), and very low half-life in soils (6 days).

Toxicity: The 96-hour LC_{50} ranges from 4,900 to 3,500,000 µg/L and the lowest value was tested on bluegill sunfish (*Lepomis macrochirus*) based on the EPA toxicity database. The toxicity EC50 values tested on aquatic plants range from 700 to 33,400 µg/L between 5 to 14 days. The lowest 5-day EC50 value was 700 µg/L tested on duckweed (*Lemna gibba*).

Water quality criteria: The CDFG has evaluated toxicological hazards to aquatic organisms but no water quality criteria were determined.

Usage: The average annual use was 24,492 lbs from 1999 to 2001 with the highest use of 33,424 lbs in 2001 and lowest use of 8,052 lbs in 1999 (Figure Glyphosate-Trim.1). The amount of use has increased. The applications are year-round but the highest use was in March and the second highest use was in July (Figure Glyphosate-Trim.2).

The average annual acreage was 26,566 acres from 1999 to 2001.

The major crops include almond (53%), uncultivated agricultural area (22%), walnut (6%), and prune (6%).

Water quality data: No concentration data are available in the SWDB database.

Conclusion: Glyphosate-trimesium is ranked as moderate risk because of its moderate toxicity to aquatic plants, the high amount of use, and winter storm application. The overall risk could be ranked as low rank if using the toxicity to aquatic animals. Glyphosate-trimesium has both very high solubility and Koc, creating a potential to contaminate sediments.

Figure Glyphosate-Trim.1

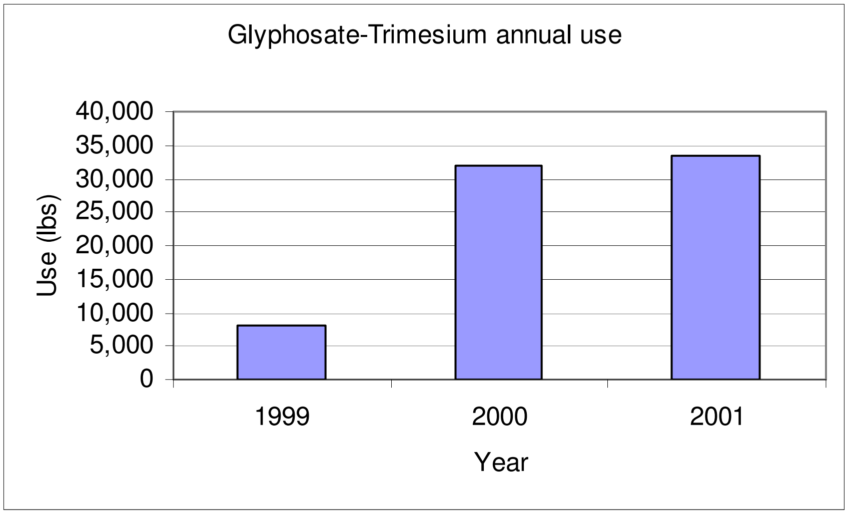
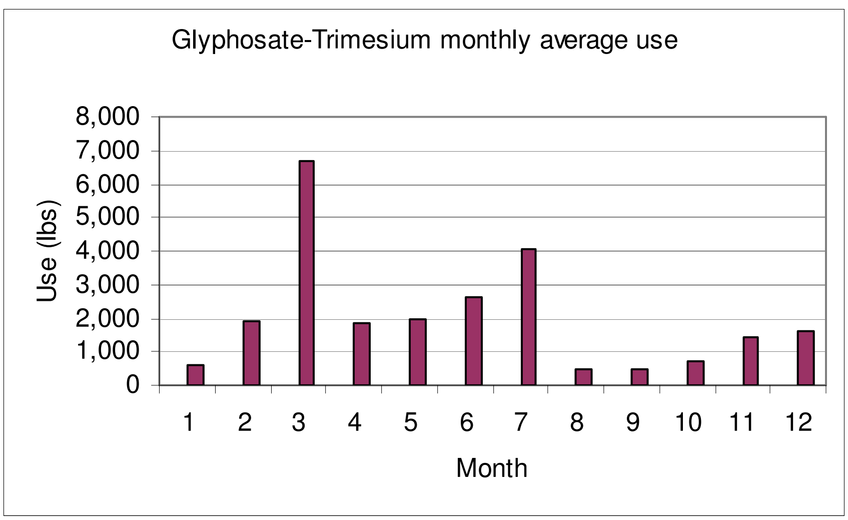


Figure Glyphosate-Trim.2



Mancozeb
Uses: Fungicide

Physical properties: Mancozeb has low water solubility (6 mg/L), high Koc (6,000), and moderate half-life in soil (43 days). Mancozeb is almost insoluble in water and most organic solvents. The half-life in water is less than 1.5 days (DPR, 2000).

Toxicity: The toxicity data showed that 96-hour LC_{50} values range from 9.5 to 2,040 μg/L. The most sensitive species was 3-day old mysid (*Mysidopsis bahia*).

Water quality criteria: There are no water quality criteria or goals proposed. The DPR has a report for environmental fate of mancozeb (DPR, 2000).

Usage: The average annual use of mancozeb is 22,125 lbs. The highest use was in 1998 and the lowest use was in 1992 (Figure Mancozeb.1). After 1998, the amount of use decreased. In 2001, the amount used was only 18% of the amount used in 1998. The high use months are between April and August with the highest use in May (Figure Mancozeb.2). The monthly uses were low from October to February.

The average annual area of mancozeb use was 16,785 acres with the highest use of 63,187 acres in 2000.

The major applications were on tomatoes for processing and canning (about 59%), onion (19%), ornamental turf (4%), apple (2%), and grapes (2%).

Water quality data: There are no concentration data for mancozeb in the SWDB.

Conclusion: Mancozeb is ranked as moderate risk to surface water quality because of its high toxicity, no heavy mancozeb applications during storm season, and reduced the amount of use in recently year. The risk to sediment is potential because of its high Koc, and moderate half-life in soils. There is a need for monitoring data.

Figure Mancozeb.1

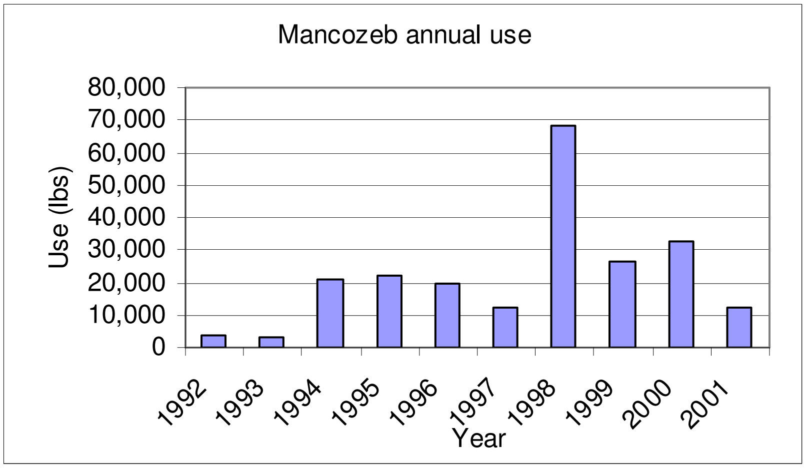
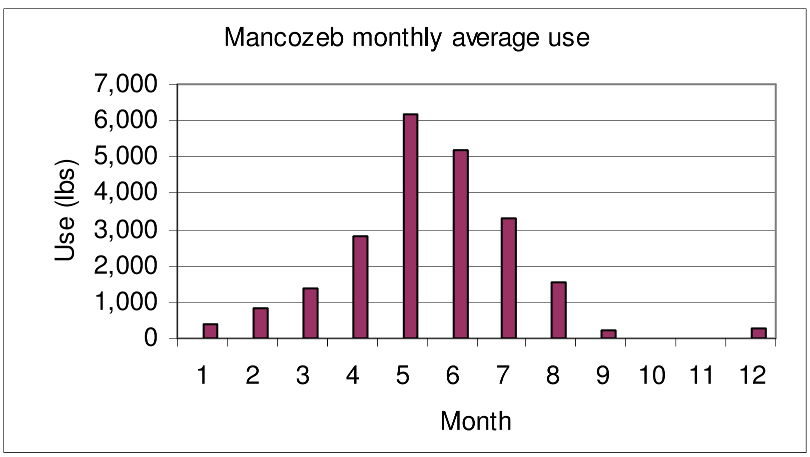


Figure Mancozeb.2



MCPA, dimethylamine salt
Uses: Herbicide.

Physical properties: MCPA has very high water solubility (866,000 mg/L), low Koc (20), and low half-life (25 days).

Toxicity: The 96-hour LC_{50} ranges from 42,000 to 306,000 μg/L (USEPA, 2003). The most sensitive species is Eastern oyster (*Crassostrea virginica*). The EC50 ranges from 170 to 122,000 μg/L for aquatic plants between 5 to 14 days. The lowest EC50 value was from a 14-day test on duckweed (*Lemna gibba*) and the lowest 5-day EC50 value was 400 μg/L.

Water quality criteria: No WQC is proposed.

Usage: The amount of use increased from 1992 to 1996, and then decreased from 1997 to 2001 (Figure MCPA.1). The highest use was 155,501 lbs in 1996. In 1998, the amount of use was 53% of the use in 1997. In 2001, the amount of use was 30,280 lbs that was lower than the amount of use in 1997. The reduction of use from 1997 to 2001 was 80%. MCPA was not on the list of the 30 highest used pesticides between 1998 and 2001. The monthly use pattern shows that the highest use was in July, and the second highest use was in June (Figure MCPA.2). During January to March, the amount of MCPA used was higher than in August to December.

The annual average area to which MCPA was applied was 120,483 acres.

The major crops on which MCPA was applied include rice (67%) and wheat (28%).

Water quality data: The SWDB database has 371 samples with MCPA concentration data, of which 32 were over the LOQ (0.1 μg/L). The highest concentration was 1.98 μg/L (Figures MCPA.3 and MCPA.4). The highest concentration was lower than lowest EC50 value (400 μg/L).

Conclusion: MCPA is ranked as moderate risk because of its moderate toxicity and low concentrations observed in surface water. Although relatively high uses of MCPA occur in the winter and high water solubility could increase the risk due to storm runoff, the observed concentrations were much lower than the lowest toxicity value. MCPA is an herbicide and its toxicity to aquatic plants is higher than to aquatic animals. Sediment contamination is unlikely because MCPA has low Koc and low half-life in soils.

Figure MCPA.1

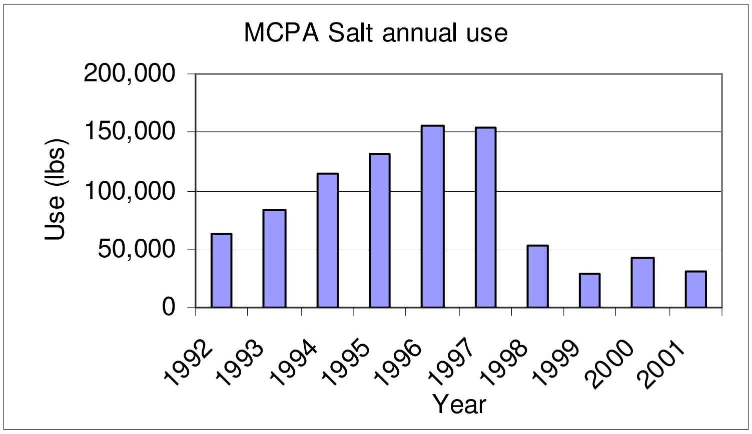


Figure MCPA.2

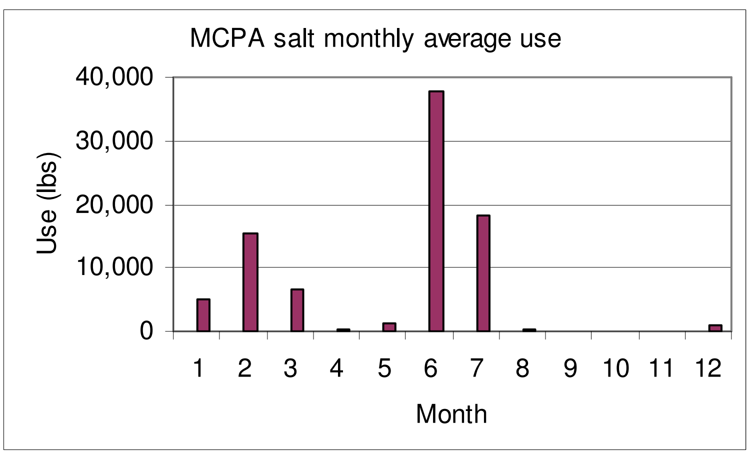


Figure MCPA.3 (zero indicates the concentration below detection limit)

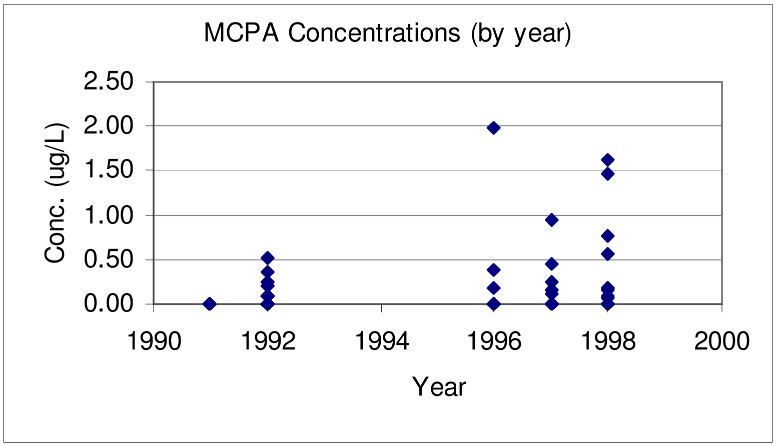
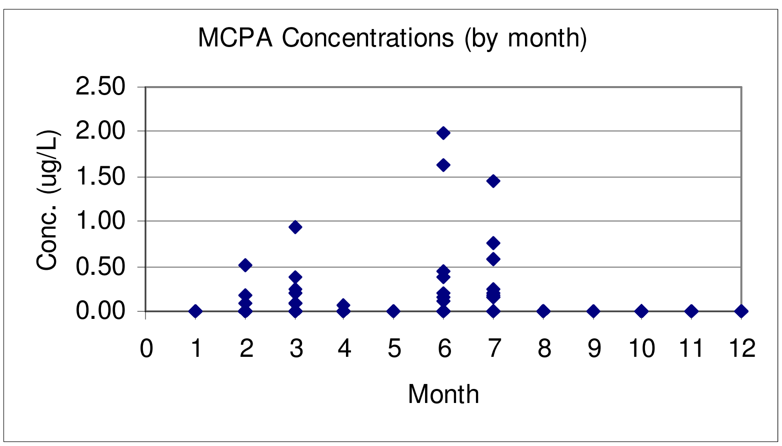


Figure MCPA.4



Metam-sodium (Metham-sodium)
Use: fumigant, fungicide, herbicide, microbiocide, and nematicide

Physical properties: Metam-sodium has a very high water solubility (963,000 mg/L), very low Koc (6), and short half-life in soil (7 days).

Toxicity: The 96-hour LC_{50} ranges from 510 to 34,100 µg/L for fishes and crustacean and no toxicity tested on aquatic plant. The lowest LC_{50} value was tested on bluegill sunfish (*Lepomis macrochirus*).

Water quality criteria: no water quality criteria for aquatic organisms available.

Usage: The average annual use was 3,404 lbs from 1992 to 2001. The amount of use varies year by year with the highest amount of use in 1996 (6,327 lbs) and the lowest use in 2001(1,114 lbs). The amount of use decreased about 78% from 1999 to 2001 (Figure Metam-sodium.1). Relatively high uses were reported to occur in March and April (Figure Metam-sodium.2).
Metam-sodium is mainly applied on tomatoes (87%) and onions (4%).

The annual average area application was 113,150 acres.

Water quality data: no concentration data are available in the SWDB.

Conclusion: Metam-sodium is ranked as moderate risk because of its moderate toxicity to aquatic organisms. The heavy usage of metam-sodium in March may pose relatively high risk due to storm runoff. Metam-sodium is unlikely to contaminate sediment because of its low Koc and short half-life in soils.

Figure Metam-sodium.1

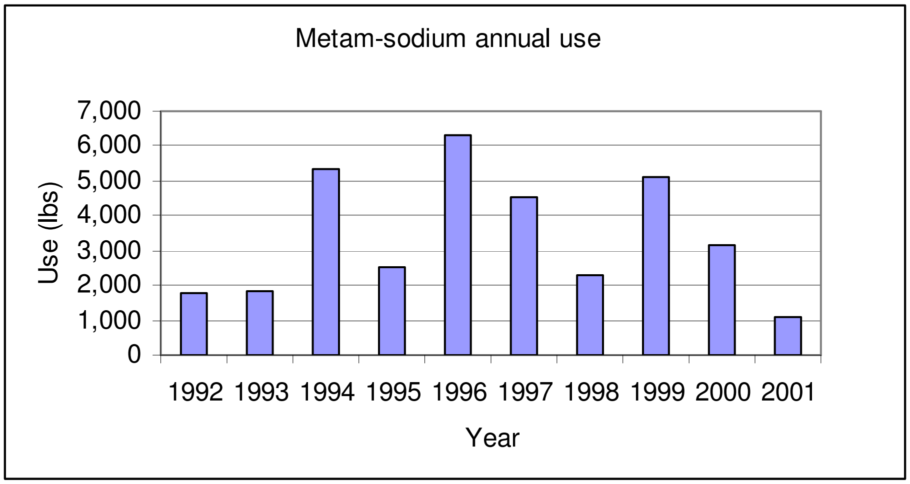
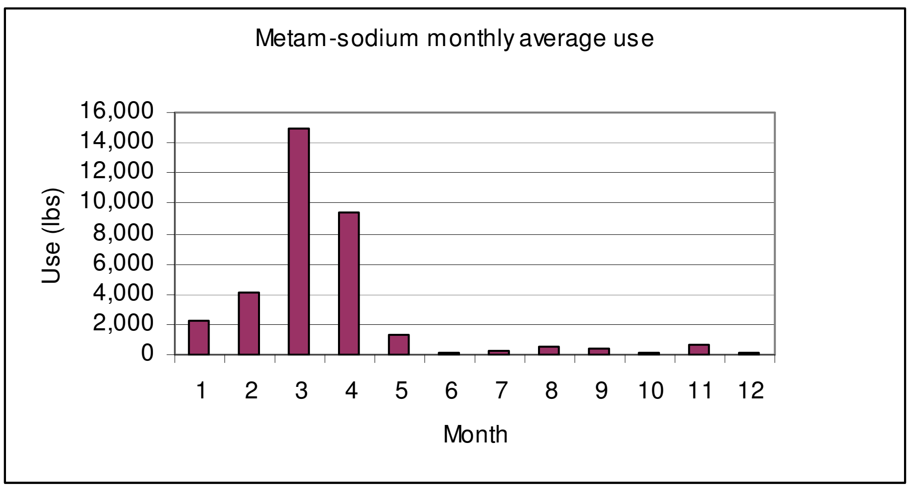


Figure Metam-sodium.2



Norflurazon

Use: Herbicide. Norflurazon was not selected in the initial targeted list because of its low uses in terms of weight and area. DPR staff suggested including it in the target list because it has been detected in the surface waters.

Physical properties: Norflurazon has a moderate water solubility (34 mg/L), moderate Koc (353), and high half-life in soil (163 days).

Toxicity: The 96-hour LC_{50} ranges from 3,800 µg/L to 16,300 µg/L for fishes and crustaceans. The lowest value was tested on eastern oyster (*Crassostrea virginica*). For mysid (*Mysidopsis bahia*), the lowest 96-hour LC_{50} was 5,530 µg/L. The EC50 ranges from 13 to 86 µg/L tested on aquatic plants between 5 and 14 days. The lowest EC50 was from a 5-day test on green algae (*Kirchneria subcapitata*).

Water quality criteria: no water quality criteria have been determined for aquatic organisms

Usage: The average annual use was 15,047 lbs from 1992 to 2001. The amounts of annual uses varied year by year. The highest use was 16,693 lbs in 1999 and the lowest use was 9,981 lbs in 1998 (Figure. Norflurazon.1). Relatively high uses were from November to February (Figure. Norflurazon.2).

Norflurazon is mainly applied on almond (56%), prune (22%), and alfalfa (12%).

The annual average area application was 12,049 acres.

Water quality data: There were 192 norflurazon concentration data in the SWDB database and 10% of data exceeded LOQ. The highest concentration was 0.98 µg/L observed in January 2001 (Figures Norflurazon.3 and 4). The highest observed concentration (0.98 µg/L) was lower than the lowest EC50 value (13 µg/L) and much lower than the lowest 96-hr LC50 (3,800 µg/L).

Conclusion: Norflurazon is ranked as moderate risk because of its high toxicity to aquatic plants and low detected concentration in surface water. The risk to surface water due to runoff is potential because norflurazon has heavy uses during the winter storm season. Norflurazon is possible to contaminate sediment because of its moderate Koc and high half-life in soils.

Figure Norflurazon.1

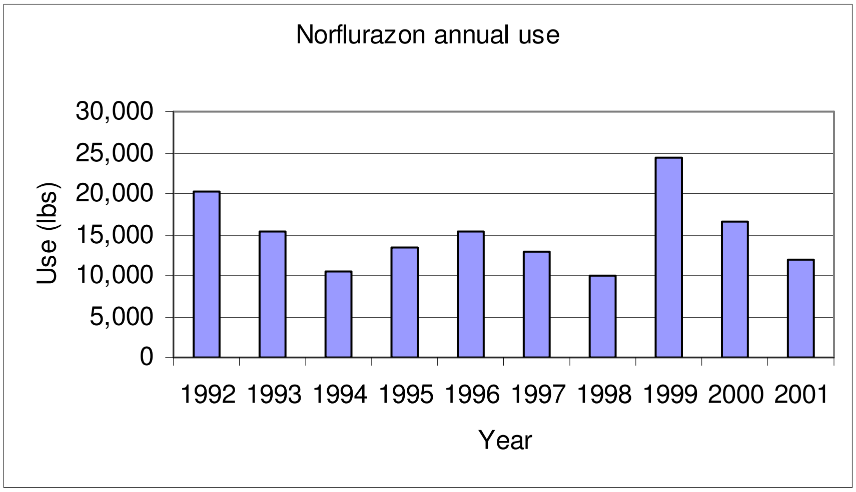


Figure Norflurazon.2

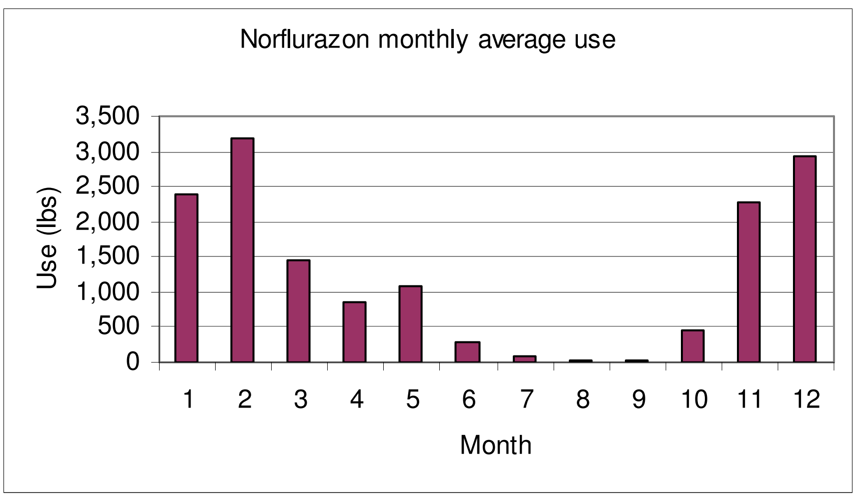


Figure Norflurazon.3 (zero indicates the concentration below detection limit)

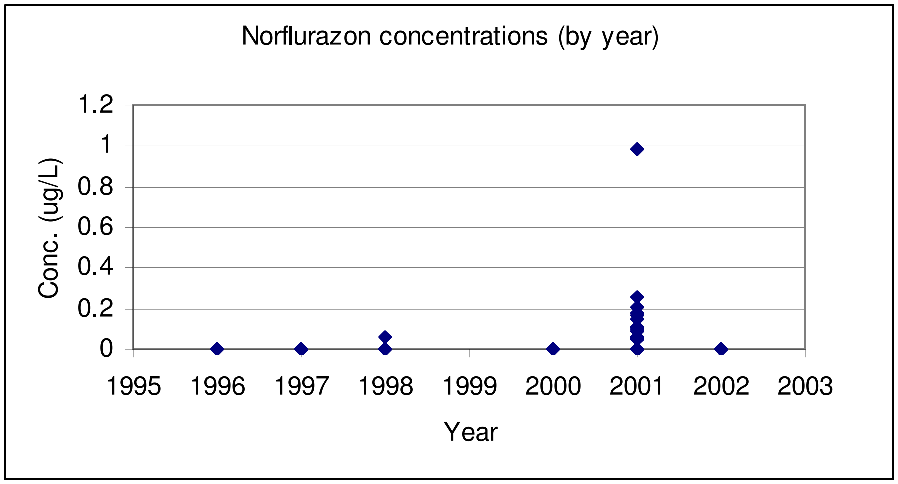
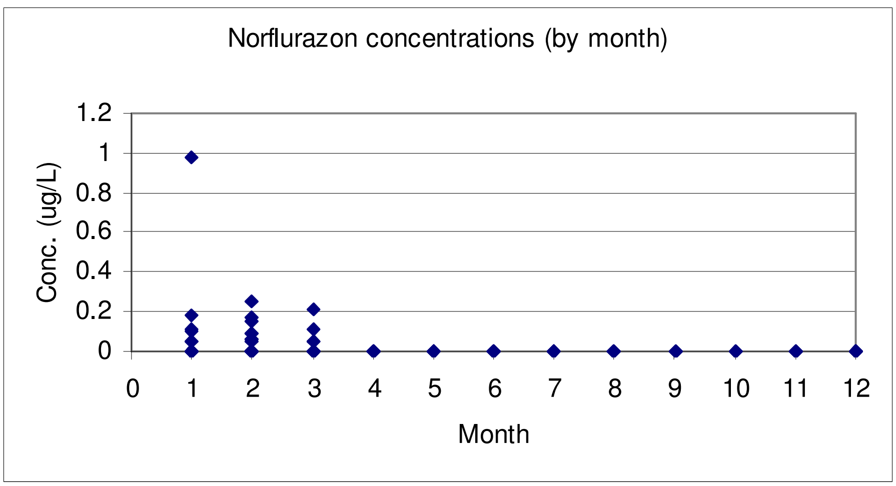


Figure Norflurazon.4



Oryzalin
<u>Uses:</u> Herbicide.

<u>Physical properties:</u> Oryzalin has low solubility (2.5 mg/L), moderate Koc (600), and low half-life in soil (20 days).

<u>Toxicity:</u> The 96-hour LC_{50} ranges from 285 to 3,450 µg/L. The most sensitive species is eastern oyster (*Crassostrea virginica*). The EC50 ranges from 15.4 to 72 µg/L tested on aquatic plants for 5 days. The lowest 5-day EC50 value was tested on duckweed (*Lemna gibba*).

<u>Water quality criteria:</u> no WQC is proposed.

<u>Usage:</u> The average annual use was 44,291 lbs from 1992 to 2001. The highest use was 60,061 lbs in 1996 and the lowest use was 3,289 lbs in 2001 (Figure Oryzalin.1). The use in 2001 was only 5% of the use in 1996. The reduction was due to the decreased use on almonds. Heavy uses occurred from November to February with the highest use in February (Figure Oryzalin.2).

The major crops include almond (59%), prune (20%), and walnut (9%) orchards.

The annual average application area was 25,742 acres.

<u>Water quality data:</u> The SWDB has 62 concentration data points, of which five were over the LOQ (LOQ ranges from 0.019 to 0.4 µg/L). The highest concentration (1.51 µg/L) was detected in November 1997. The highest observed concentration (1.51 µg/L) was lower than the lowest EC50 value (15.4 µg/L) tested on aquatic plants and much lower than the lowest LC50 value (285 µg/L).

<u>Conclusion:</u> Oryzalin is ranked as moderate risk to surface water because of its high toxicity to aquatic plants and low observed concentrations in surface waters. The toxicity of oryzalin to aquatic animals is lower than the toxicity to aquatic organism. The risk could be lower because the amount of use decreased in recent years. Although the major amount of oryzalin is applied during the winter storm season, the low water solubility may not result in high concentrations in surface water. However, sediment contamination may occur because of the moderate Koc. Low half-life in soil may reduce the risk of sediment contamination.

Figure Oryzalin.1

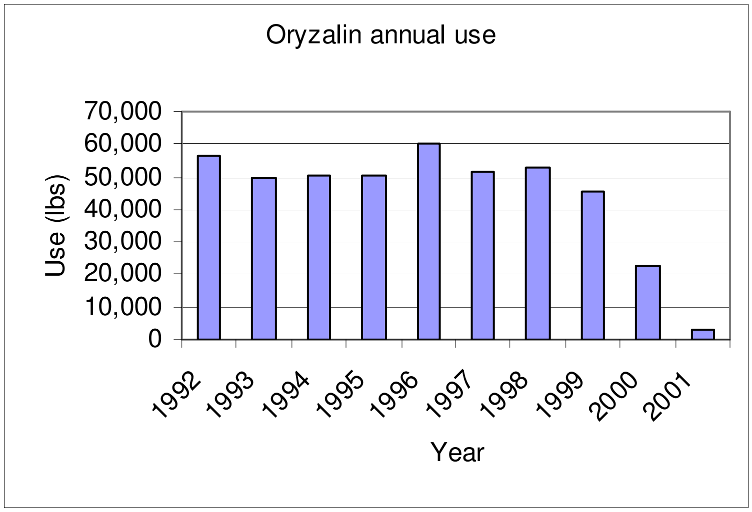


Figure Oryzalin.2

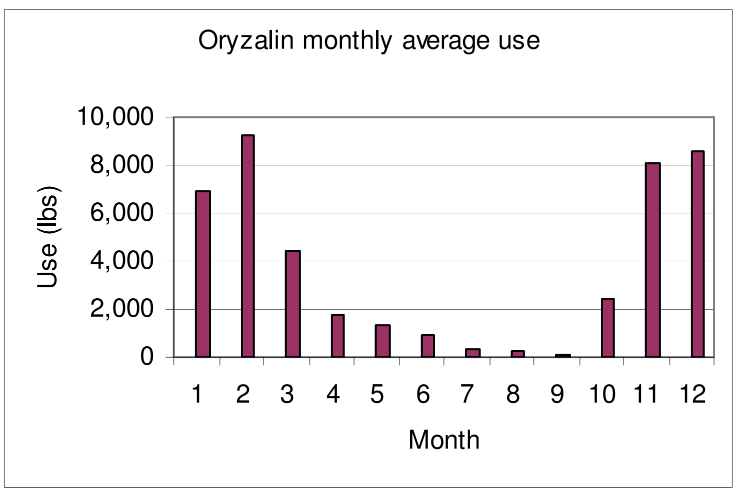


Figure Oryzalin.3 (zero indicates the concentration below detection limit)

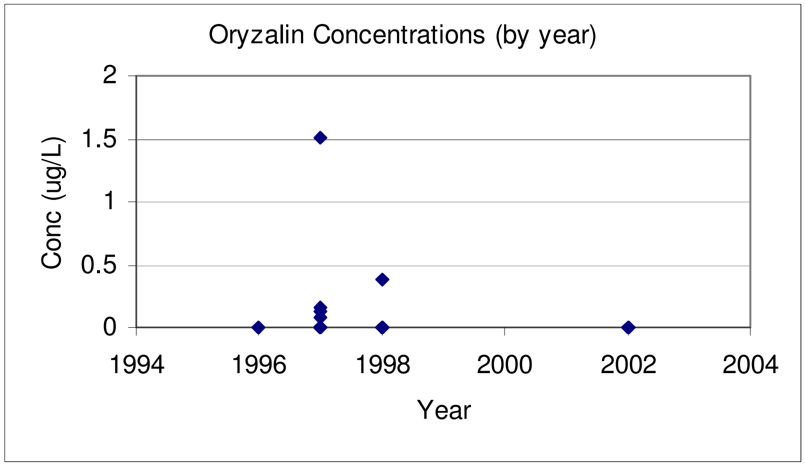
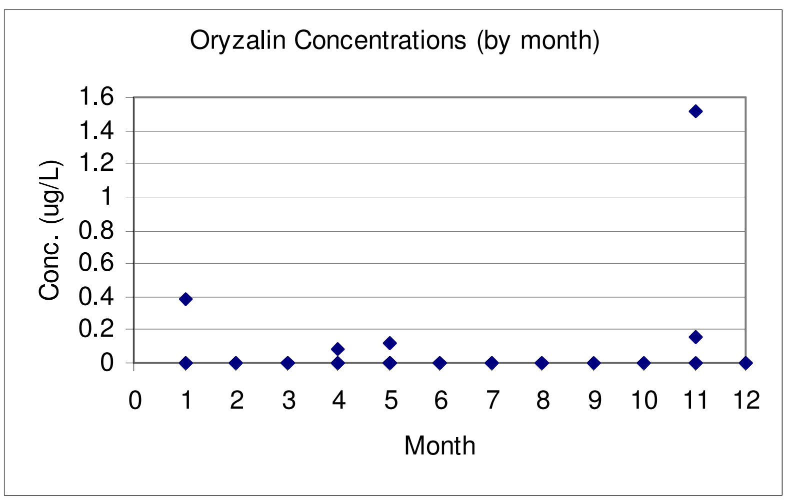


Figure Oryzalin.4



Phosmet
Uses: Insecticide.

Physical properties: Phosmet has moderate water solubility (20 mg/L) and Koc (820), and low half-life in soil (19 days).

Toxicity: The 96-hour LC_{50} ranges 2.0 to 10,600 µg/L. The lowest value was tested on scud (*Gammarus fasciatus*). The 96-hour LC_{50} value tested on mysid (*Mysidopsis bahia*) was 16 µg/L.

Water quality criteria: There are no water quality criteria or goals proposed.

Usage: The average annual use is 40,298 lbs from 1992 to 2001 with the highest use of 71,583 lbs in 1997 and lowest use of 9,059 lbs in 1992 (Figure Phosmet.1). The annual uses increased in the recent years. The monthly use pattern shows relatively high uses between May and July (Figure Phosmet.2). The highest use was in July. There were no uses in October and November.

The average annual area of application was 16,876 acres with the highest acreage applied in 1997.

The major uses are on walnut (51%), almond (16%), apple (10%), and alfalfa (9%).

Water quality data: There were 685 samples with phosmet concentration data in the SWDB and none of the concentrations were over the LOQ (0.05 to 1 µg/L). The concentration data were collected from 1992 to 2000.

Conclusion: Phosmet is ranked as moderate risk to surface water quality. Although phosmet has high toxicity and relatively high use in recent years, the observed concentrations were below the LOQ and major application time was not in the winter storm season. In addition, phosmet has high degradation rate in water (18 hours at pH 7, EXTOXNET). Sediment contamination is possible because of the moderate Koc and low soil half-life.

Figure Phosmet.1

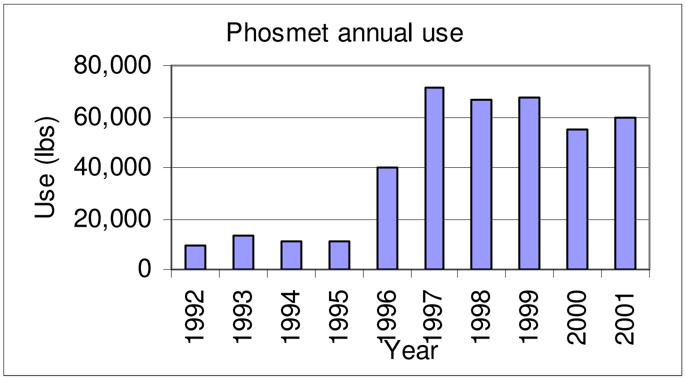
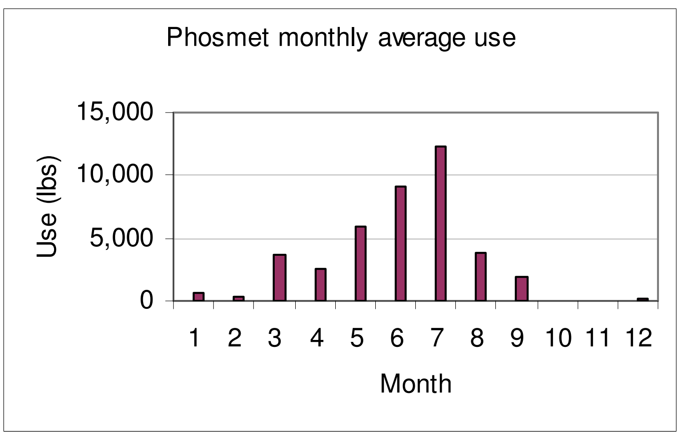


Figure Phosmet.2



Propiconazole
Uses: Fungicide.

Physical properties: Propiconazole has high water solubility (110 mg/L), moderate Koc (650), and long half-life in soil (115 days).

Toxicity: The 96-hour LC_{50} ranged 510 to 49,000 µg/L. The most sensitive species was mysid (*Mysidopsis bahia*)

Water quality criteria: no WQC is proposed.

Usage: Propiconazole has been applied to crops since 1997. The annual average use was 9,875 lbs and the highest use was 19,556 lbs in 1998 and lowest use was 949 lbs in 2001 (Figure Propiconazole.1). The reduction was about 95% from 1998 to 2001. The major reduction was due to the decrease of applications on almonds. The monthly use shows that heavy uses occurred in February and March (Figure Propiconazole.2).

The major crops on which propiconazole are applied are almond (57%), prune (30%), and peach (12%).

The average annual area to which propiconazole was applied was 78,111 acres.

Water quality data: No concentration data are available in the DPR SWDB database.

Conclusion: Propiconazole is ranked as moderate risk because of its moderate toxicity, application time (winter storm season), and decreased annual uses. Sediment contamination is possible because of the moderate Koc and the long half-life in soils.

Figure Propiconazole.1

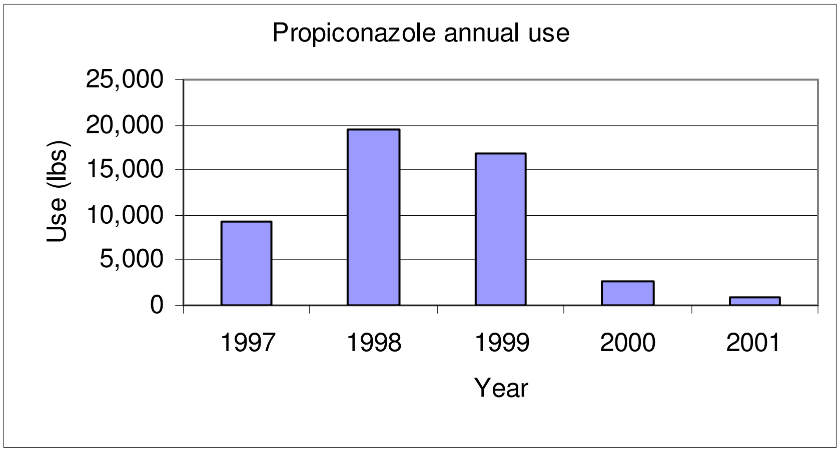
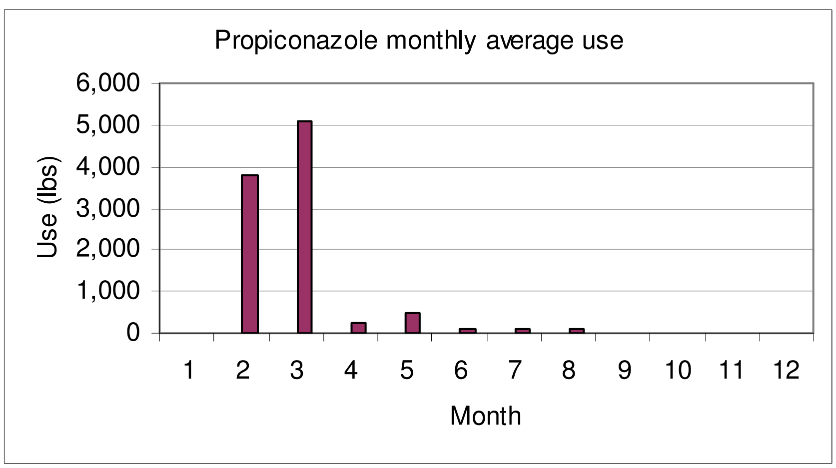


Figure Propiconazole.2



Simazine

Uses: Herbicide. Simazine was one of the initial targets because of its low uses in terms of both weight and area. The DPR staff recommended including it in the target list because it has been detected in the Sacramento River watershed.

Physical properties: Simazine has low solubility (6.2 mg/L), moderate Koc (130), and moderate half-life (60 days) in soil.

Toxicity: The 96-hour LC_{50} ranges from 4,300 to 1,000,000 µg/L tested on aquatic animals. The most sensitive species was sheepshead minnow (*Cyprinodon variegates*). The EC50 ranges from 36 to 5,000 µg/L tested on aquatic plants between 5 and 14 days. The lowest EC50 value was from a 5-day test on bluegreen algae (*Anabaena flos-aquae*).

Water quality criteria: The CDPR reviewed the environmental fate of simazine in 2004 but no WQC is determined.

Usage: The annual average of simazine use was 21,132 lbs from 1992 to 2001. The highest amount of use was 31,791 lbs in 1992 and the lowest amount of use was 15,585 lbs in 2001 (Figure Simazine.1). The reduction was 51% from 1992 to 2001. The monthly uses vary broadly but the monthly uses in winter were much higher than in summer (Figure Simazine.2). The highest uses were between November and March and the lowest use was in September.

The average annual area of use was 20,019 acres.

The major crops to which simazine has been applied include walnut (50%), almond (32%), olive (11%), and pear (1%) orchards.

Water quality data: The DPR SWDB has 1,707 samples with simazine concentration data and none of them exceeded the lowest toxicity concentration. The highest concentration was 6.1 µg/L observed in April 1996 (Figures Simazine.3 and Simazine.4). The highest observed concentration (6.1 µg/L) was much lower than the lowest LC50 (4,300 µg/L) and EC50 (36 µg/L).

Conclusion: Simazine is ranked as low risk for the surface water quality because of its low toxicity, low detected concentrations, and low solubility. The risk to contaminate surface water may be higher because of relatively high uses during the winter storm season. In recent years, simazine uses have been reduced. Simazine is highly toxic to aquatic plants. Sediment contamination is possible because of its moderate Koc and half-life in soils.

Figure Simazine.1

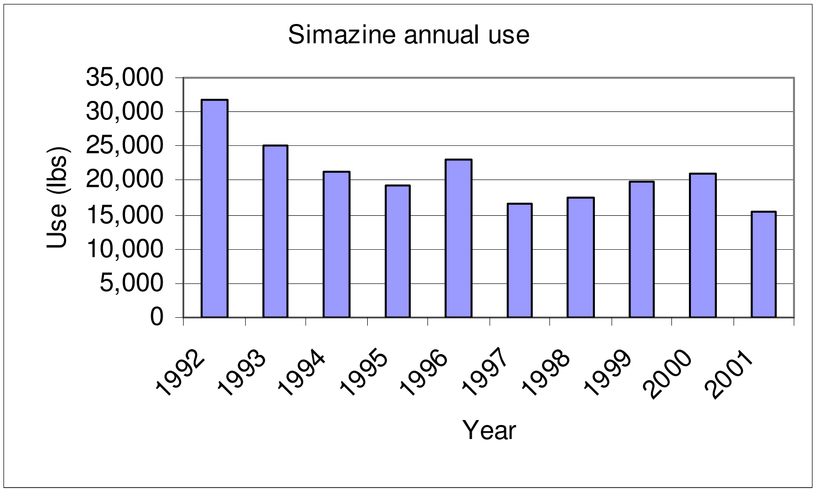


Figure Simazine.2

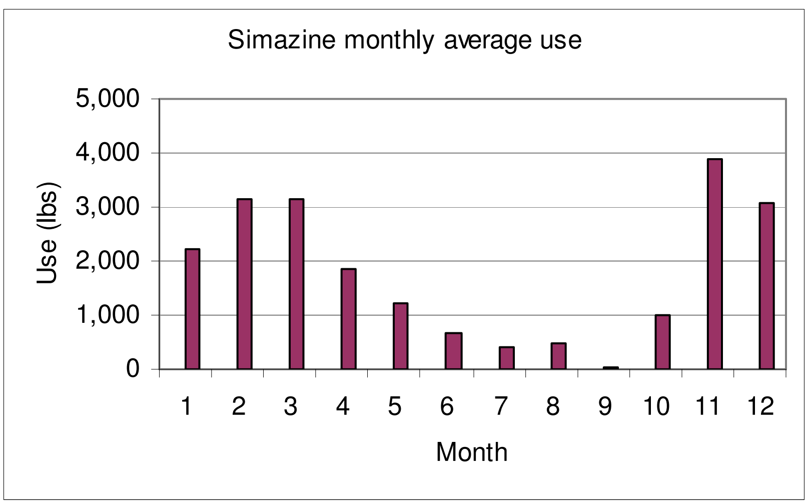


Figure Simazine.3 (zero indicates the concentration below detection limit)

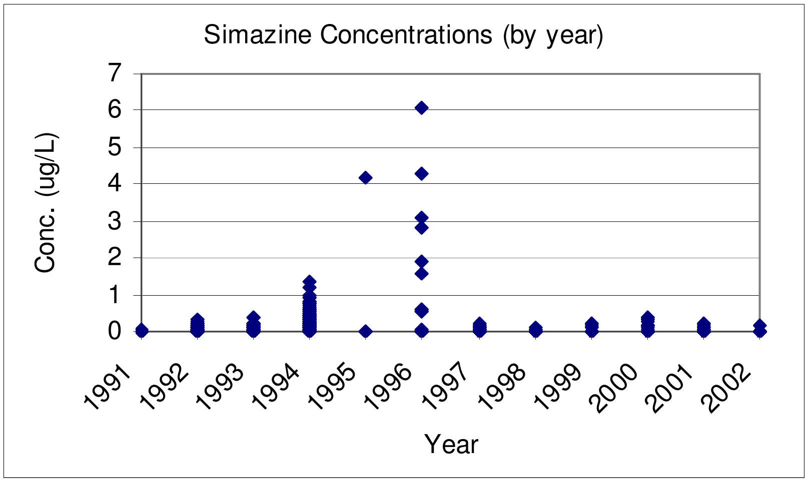
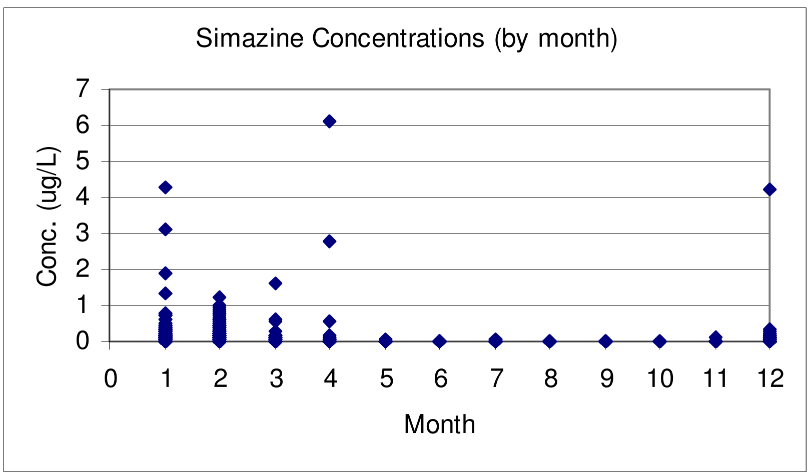


Figure Simazine.4



Appendix C. Low Relative Risk Pesticides

Azoxystrobin
Use: Fungicide.

Physical properties: Azoxystrobin has a moderate water solubility (10 mg/L), moderate Koc (581), and high half-life in soil (112 days).

Toxicity: The 96-hour LC_{50} ranges from 56,000 to 1,100,000 µg/L. The lowest value was tested on mysid (*Mysidopsis bahia*).

Water quality criteria: not available

Usage: The average annual use was 10,737 lbs from 1997 to 2001 and no uses were reported before 1997. The annual uses increased from 1997 to 2001, with the highest amount used in 2000 and the lowest amount used in 1997 (Figure. Azoxystrobin.1). The monthly use showed that azoxystrobin was used from April to September, with the highest use in July (Figure. Azoxystrobin.2).

Azoxystrobin is applied on rice (39%), almond (34%), and tomato (15%).

The annual average area application was 63,446 acres.

Water quality data: no data available

Conclusion: Azoxystrobin is ranked as low risk for the surface water quality because of its low toxicity. Although the risk of winter storm runoff is low because of no winter season application, the irrigation runoff from fields may be a potential risk. The risk may be increased because of the annual uses have increased in recent years. The risk to sediment contamination is possible because of its moderate Koc and long half-life in soils.

Figure Azoxystrobin.1

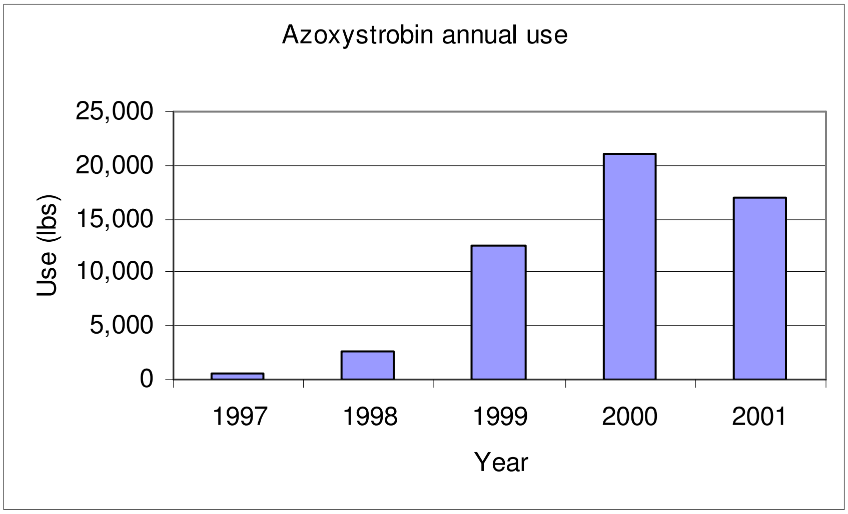
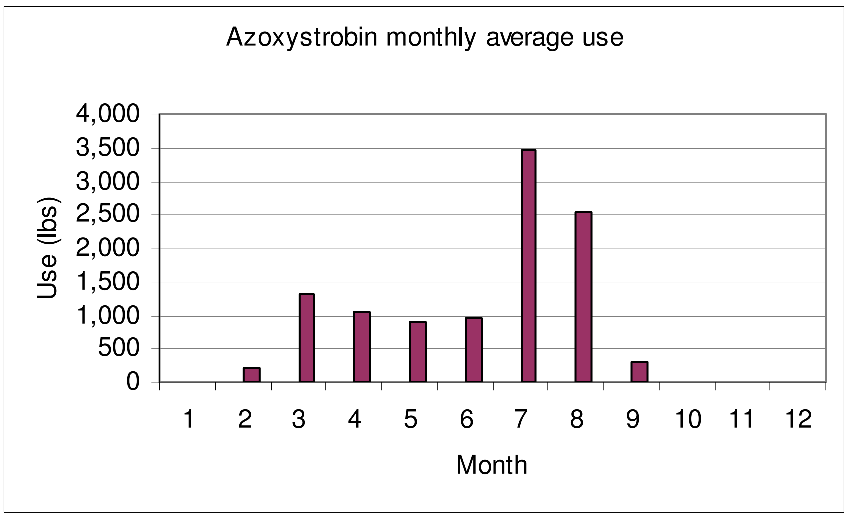


Figure Azoxystrobin.2



Copper Oxychloride Sulfate
Use: Fungicide.

Physical properties: No water solubility, Koc, or half-life for copper sulfate is available in the ARS and EXTOXNET databases.

Toxicity: The 96-hour LC_{50} are 3,750 µg/L and 180,000 µg/L. The lowest value was tested on rainbow trout (*Oncorhynchus mykiss*).

Water quality criteria: No WQC is determined.

Usage: The average annual use was 13,130 lbs from 1992 to 2001. The highest amount used was 33,143 lbs in 1995 and lowest use was 100 in 2001 (Figure. Coppersulfate.1). The highest use was in January (Figure. Coppersulfate.2).

The major application of copper sulfate is on peach (62%) and pear (22%).

The annual average area application was 34,689 acres.

Water quality data: No water quality data are available.

Conclusion: Copper sulfate is ranked as low risk for the surface water quality because it has low rank of toxicity. The risk to sediment contamination is possible because copper is strong adsorbed to soil particles.

Figure CopperSulfate.1

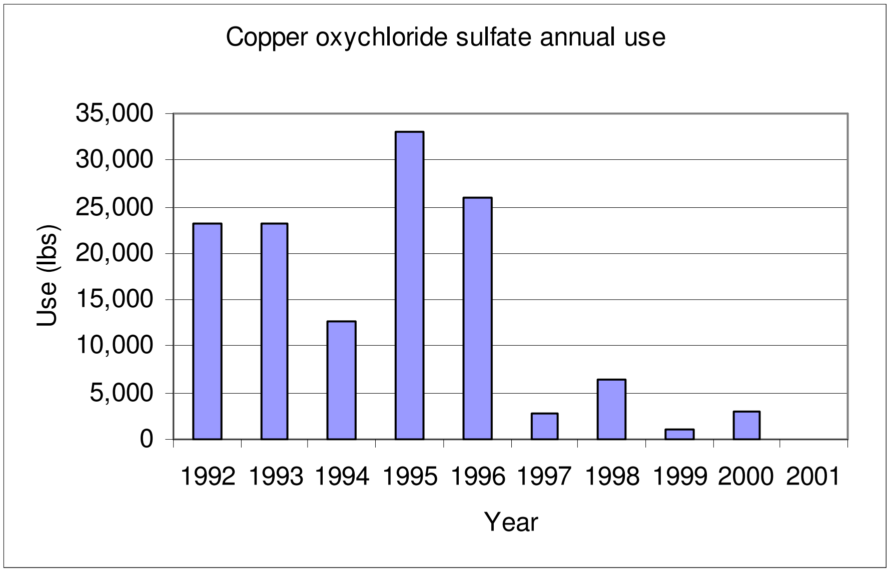
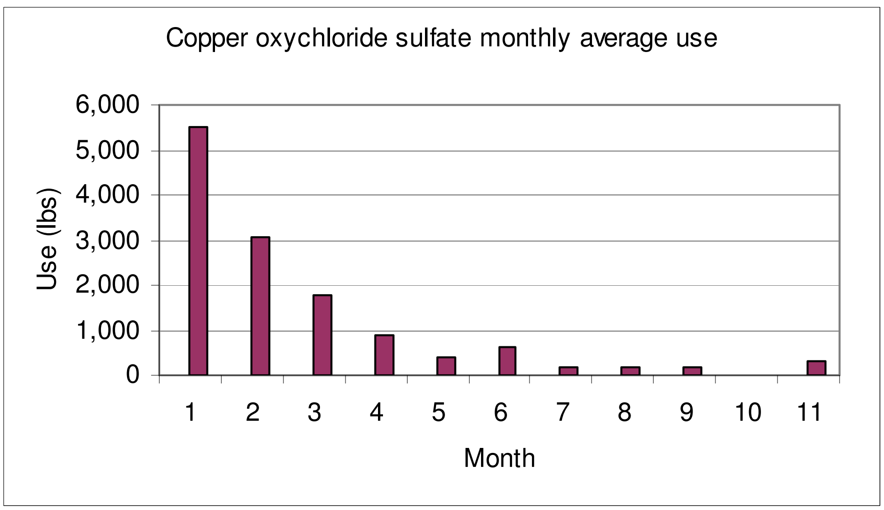


Figure CopperSulfate.2



EPTC
Uses: Herbicide.

Physical properties: EPTC has high solubility (344 mg/L), moderate Koc (200), and very low half-life (6 days) in soil.

Toxicity: The 96-hour LC_{50} ranges from 11,500 to 180,000 µg/L with the lowest toxicity tested on trout (*Salvelinus namaycush*). The EC50 ranges from 1,400 to 41,000 µg/L tested on aquatic plants between 72 and 96 hours. The lowest EC50 value was from a 96-hour test on green algae (*Selenastrum capricornutum*).

Water quality criteria: no WQC is proposed

Usage: The average annual reported use is 31,070 lbs from 1992 to 2001. The highest amount used was 58,535 lbs in 1993 and the lowest amount used was 9,719 lbs in 2001 (Figure EPTC.1). Since 1994 the amount of use has decreased, the amount of use in 2001 was only 17% of the amount used in 1993. EPTC was not on the list of the 30 highest used pesticides from 1998 to 2001. Months of high reported use are between April and July, with the highest use in June (Figure EPTC.2). There was no reported EPTC use in December and January.

The average annual area to which EPTC applied was 10,599 acres.

The major uses are on beans (32%), sugarbeet (20%), alfalfa (12%), safflower (10%), and almond (9%).

Water quality data: The SWDB has 534 EPTC concentration data, 31 of them exceeded the LOQ (LOQ was in range of 0.05 to 0.1 µg/L) (Figures EPTC.3 and EPTC.4). The highest concentration was 0.716 µg/L.

Conclusion: EPTC is ranked as low risk for the surface water quality because of low ranked toxicity, low detection in surface water, and decreased annual use. EPTC is slightly toxic to aquatic animals. Although EPTC is an herbicide, it has relatively low toxicity to aquatic plants. Sediment contamination is possible because of its moderate Koc and low half-life in soil.

Figure EPTC.1

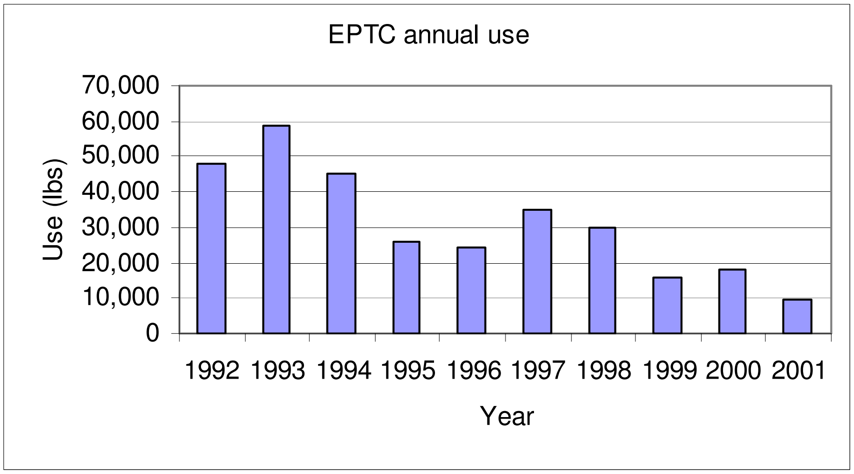


Figure EPTC.2

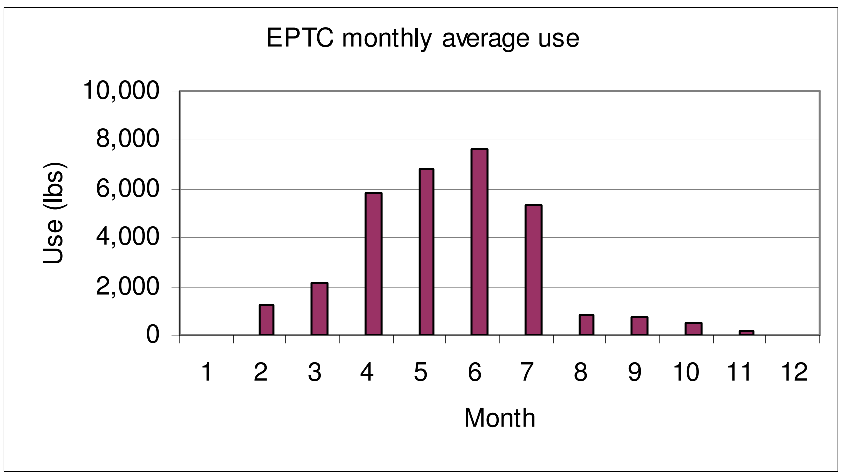


Figure EPTC.3 (zero indicates the concentration below detection limit)

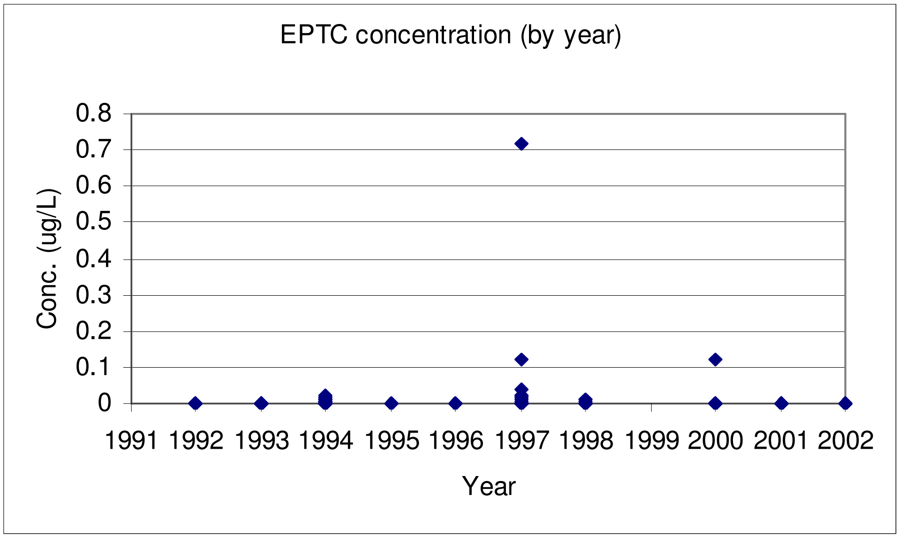
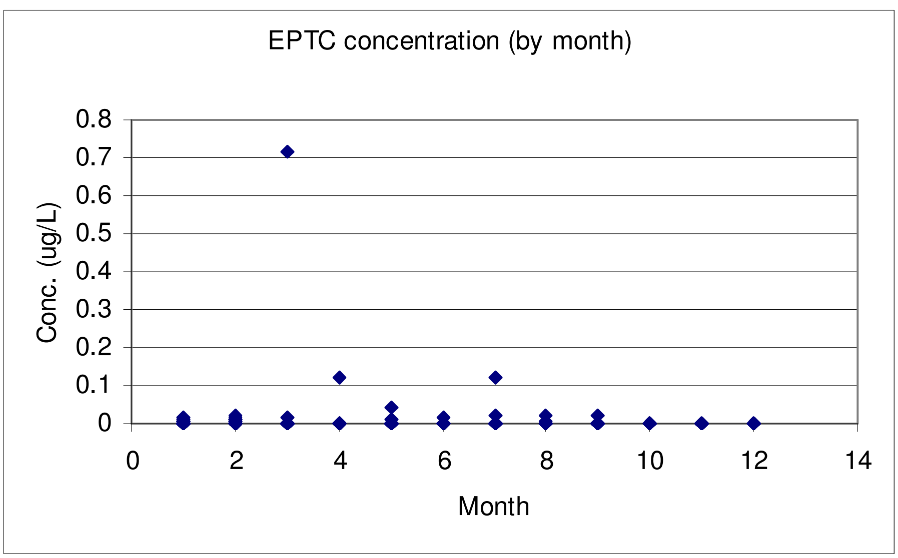


Figure EPTC.4



Glyphosate
Uses: Herbicide.

Physical properties: Glyphosate has very high water solubility (900,000 mg/L), very high Koc (24,000), and moderate half-life in soils (47 days).

Toxicity: The 96-hour LC_{50} ranges from 1,300 to 1,000,000 µg/L and the lowest value was tested on rainbow trout (*Oncorhynchus mykiss*) based on the EPA toxicity database (USEPA, 2003). The EC50 ranges from 770 to 38,600 µg/L tested on aquatic plants between 48 hours to 14 days. The lowest EC50 value was from a 7-day test on marine diatom (*Skeletonema costatum*) and the 4-day EC50 was 11,750 µg/L tested on blue-green algae (*Anabaena flos-aquae*).

Water quality criteria: The CDFG has evaluated toxicological hazards to aquatic organisms but no water quality criteria were determined.

Usage: The average annual use of glyphosate was 229,896 lbs from 1992 to 2001 with the highest use of 313,173 lbs in 1998 and lowest use of 138,448 lbs in 1992 (Figure Glyphosate.1). The amount of use increased from 1992 to 1998 but decreased after 1998. In 2001, the amount of use was 252,758 lbs that was 183% of the amount used in 1992 and 81% of used in 1998. The application of glyphosate is year-round but the relatively high uses were in February, March, and June to August (Figure Glyphosate.2).

The average annual acreage was 398,707 acres from 1992 to 2001.

The major crops include almond (38%), walnut (16%), prune (10%), and tomato (8%).

Water quality data: No concentration data are available in the SWDB database.

Conclusion: Glyphosate is ranked as low risk because of its low toxicity. The risk could be higher because of the high amount of use and applied in winter storm season. Although glyphosate is an herbicide, the toxicity to aquatic plants is relatively low. Glyphosate has both high solubility and high Koc, creating a relatively high potential to contaminate surface water and sediments.

Figure Glyphosate.1

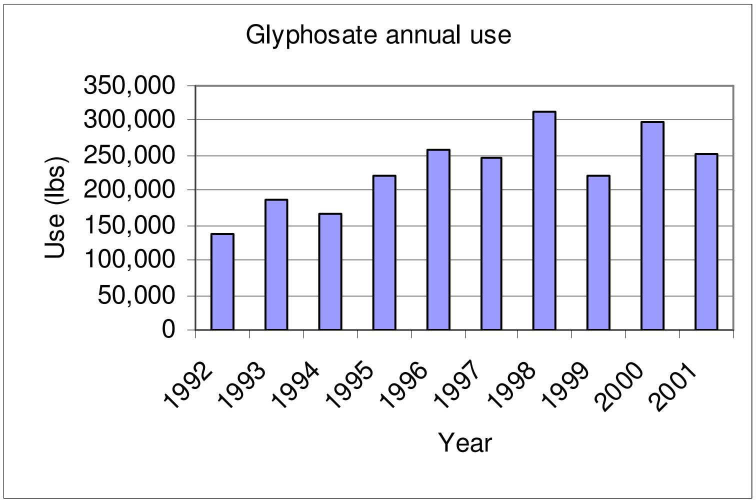
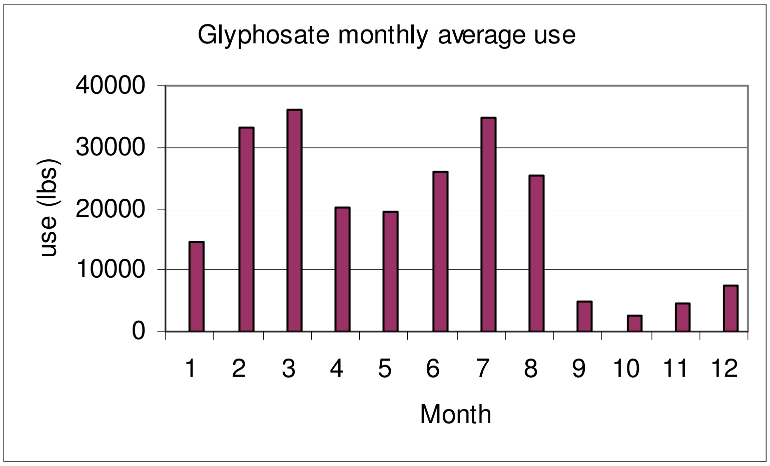


Figure Glyphosate.2



Iprodione
Uses: Fungicide.

Physical properties: moderate water solubility (13.9 mg/L), moderate Koc (700), and low half-life (14 days) in soil.

Toxicity: The 96-hour LC_{50} values for iprodione range from 2,300 to 7,800 µg/L (USEPA, 2003). The most sensitive species is Eastern oyster (*Crassostrea virginica*).

Water quality criteria: no WQC is proposed.

Usage: The average annual use was 39,685 lbs with the highest use in 1995 and the lowest use in 2001 (Figure Iprodione.1). From 1992 to 1995, the amount of use increased but from 1996 to 2001, the amount of use decreased. Iprodione was not on the list of the 30 highest used pesticides from 1998 to 2001. In 2001, the amount of use was 11,675 lbs that was only 15% of the amount reportedly used in 1995. The months with the heaviest uses were in February and March (Figure Iprodione.2).

The average annual area of reported use was 70,799 acres.

The major uses of pesticide are on almond (42%), prune (36%), and peach (17%) orchards.

Water quality data: There are no concentration data available for iprodione in the SWDB database.

Conclusion: Iprodione is ranked as low risk because of its low toxicity and decreased annual uses. However, the risk to surface water quality might be increased because of heavy uses are in the winter storm season. Sediment contamination may be possible but is not likely to pose a high risk because of iprodione's low toxicity, moderate Koc, and low soil half-life.

Figure Iprodione.1

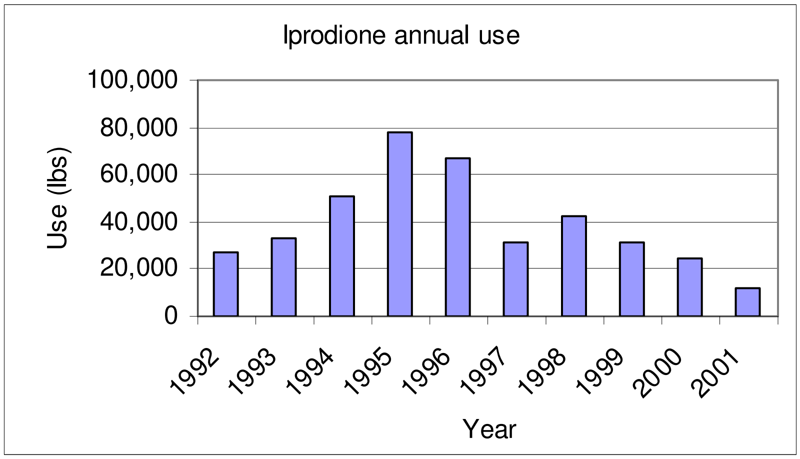
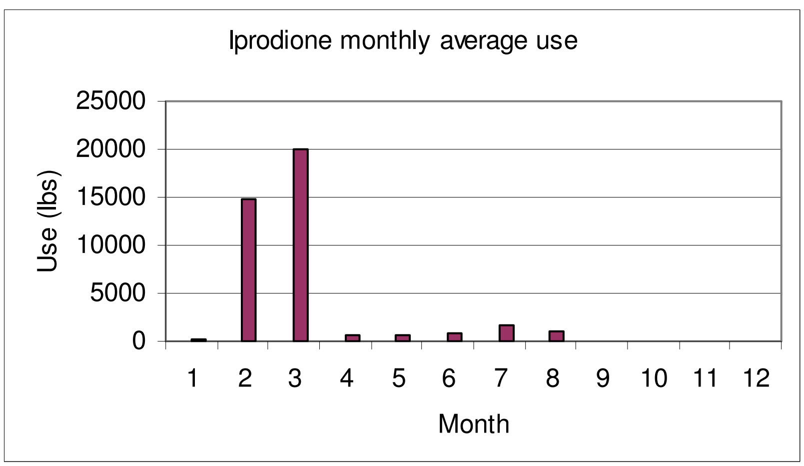


Figure Iprodione.2



Methyl bromide
Uses: Gaseous fungicide.

Physical properties: Methyl bromide has very high water solubility (13,400 mg/L), low Koc (22), and moderate half-life (55 days).

Toxicity: The toxicity database has no 96-hour LC_{50} data for methyl bromide but it has one 48-hour EC_{50} (2,600 µg/L) that was tested on the water flea (*Daphnia magna*).

Usage: The use of methyl bromide showed a significant decrease from 1999 (Figure MethylBromide.1). The USEPA scheduled the phase-out of methyl bromide use by 2000 but the amount of use was 137,754 lbs in 2001 that was about 17% of the amount used in 1995. The highest reported uses were from September to November with the highest use in October (Figure MethylBromide.2).

The average annual area to which methyl bromide was applied was 6,359 acres.

The major crops include peach (25%), walnut (23%), prune (19%), and almond (5%) orchards.

Water quality data: There are no methyl bromide concentration data in the SWDB.

Conclusion: Methyl bromide is ranked as low risk for the surface water quality because it has low toxicity and it was reportedly phased out. Sediment contamination risk is unlikely because of its low Koc and moderate half-life in soil.

Figure MethylBromid.1

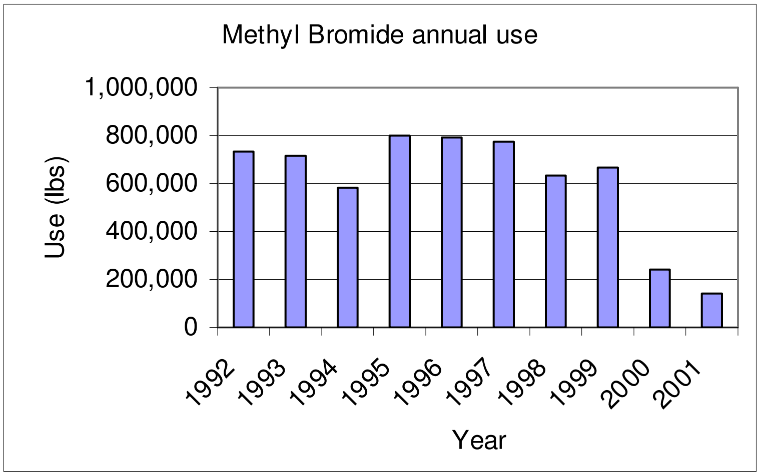
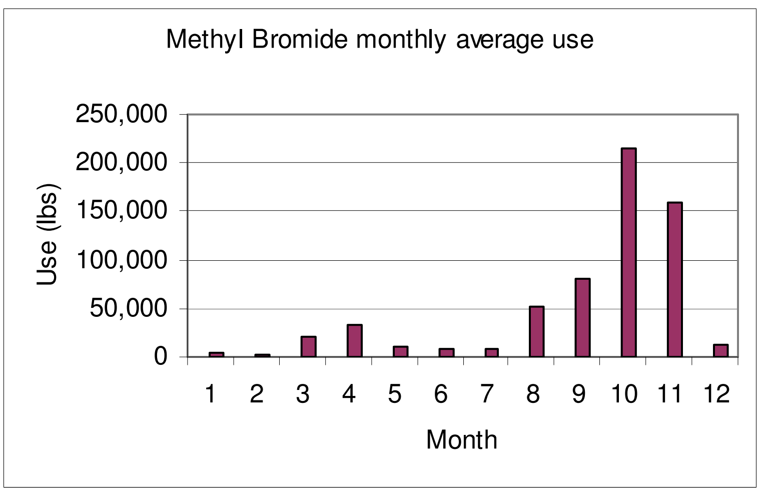


Figure MethylBromid.2



Triclopyr, triethylamine salt
Uses: Herbicide.

Physical properties: Triclopyr, triethylamine salt has very high water solubility (2,100,000 mg/L), low Koc (20), and moderate half-life in soil (46 days)

Toxicity: The 96-hour LC_{50} values range from 58,000 to 1,000,000 µg/L. The lowest value was tested on Eastern oyster (*Crassostrea virginica*). The EC50 ranges from 5,900 to 39,100 µg/L tested on aquatic plants between 4 and 14 days. The lowest 120-hour EC50 value was 14,900 µg/L tested on marine diatom (*Skeletonema costatum*).

Water quality criteria: no WQC is proposed.

Usages: The annual average use was 28,069 lbs from 1992 to 2001 but the annual use from 1992 to 1995 was below 200 lbs. The amount of use increased from 1996 to 2000 but in 2001, amount of use slightly decreased (Figure Triclopyr.1). The highest annual use was 76,216 lbs in 2000. The monthly use pattern shows that the high uses were in June and July, and very low applications were in other months (Figure Triclopyr.2).

The annual average application area was 83,496 acres.

The major use was on rice (about 99%).

Water quality data: There were no concentration data available for triclopyr.

Conclusion: Triclopyr, triethylamine salt is ranked as low risk because of its low toxicity. Triclopyr is an herbicide but its lowest toxicity value (120-hour EC50) on aquatic plants was lower than the 96-hour LC50 tested on aquatic animals. Therefore, the lowest 96-hour LC50 was used to determine the toxicity rank. The runoff of triclopyr from the rice fields may be a concern because of its high water solubility. Sediment contamination is ranked as low risk because of the low Koc and moderate soil half-life.

Figure Triclopyr.1

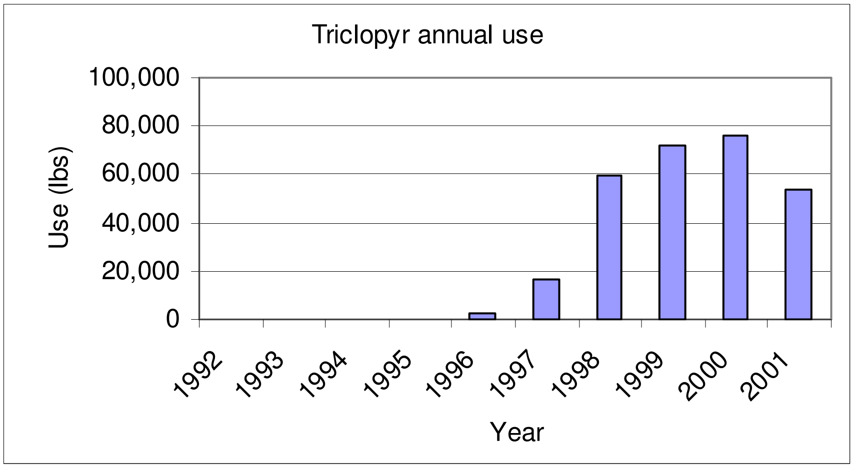
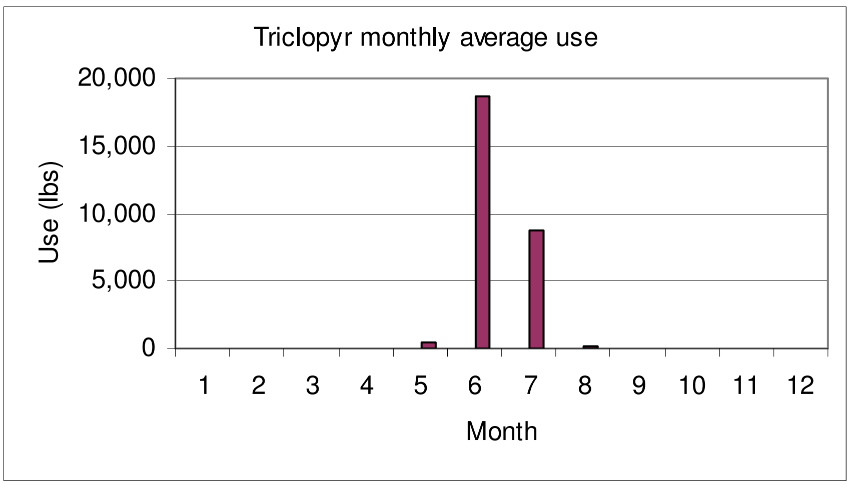


Figure Triclopyr.2



Triforine
Uses: Fungicide and insecticide.

Physical properties: Triforine has low water solubility (6 mg/L), moderate Koc (527), and low soil half-life (21 days) in field.

Toxicity: There are no 96-hour LC_{50} reported in the EPA toxicity database, and the 48-hour EC50 are from 21,400 to 1,000,000 μg/L. The lowest 48 hour EC_{50}, 221,400 μg/L was tested on rainbow trout (*Oncorhynchus mykiss*).

Water quality criteria: no WQC is determined

Usage: The annual average use was 9,706 lbs. The highest use was 31,832 lbs in 1993 and the lowest use was only one pond in 2000 (Figure Triforine.1). From 1993, the amount of use decreased significantly. From 1998, there were almost no uses based on the DPR PUR database. Therefore, triforine was not on the list of 30 highest used pesticides between 1998 and 2001. The monthly use showed that the highest use is in March (Figure Triforine.2).

The annual average area applied was 31,438 acres but there have been almost no uses after 1998.

The major applications were on peach (57 %) and prune (40%).

Water quality data: The DPR SWDB does not have any triforine concentration data.

Conclusion: Triforine is ranked as low risk because of its low toxicity and significant reduced use. The risk of runoff was relatively high in March because the highest use of triforine. The sediment contamination is possible because of its moderate Koc.

Figure Triforine.1

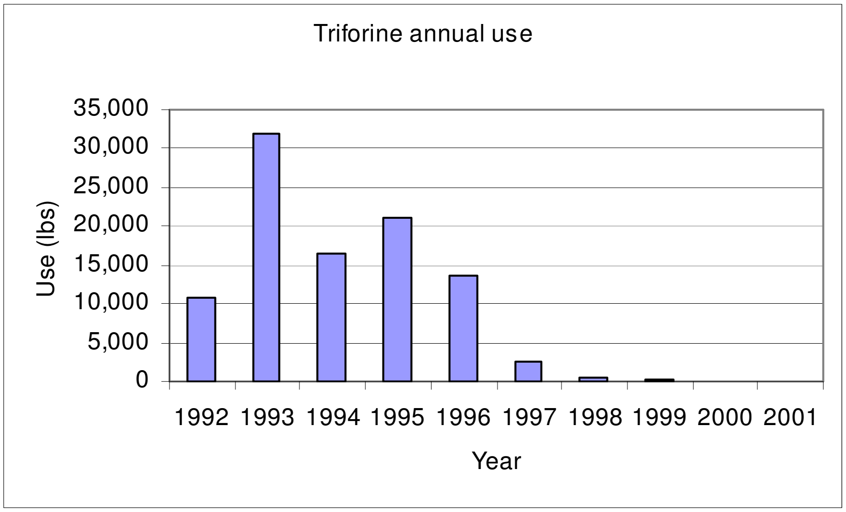


Figure Triforine.2